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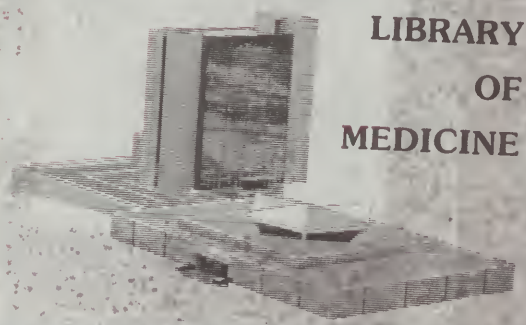

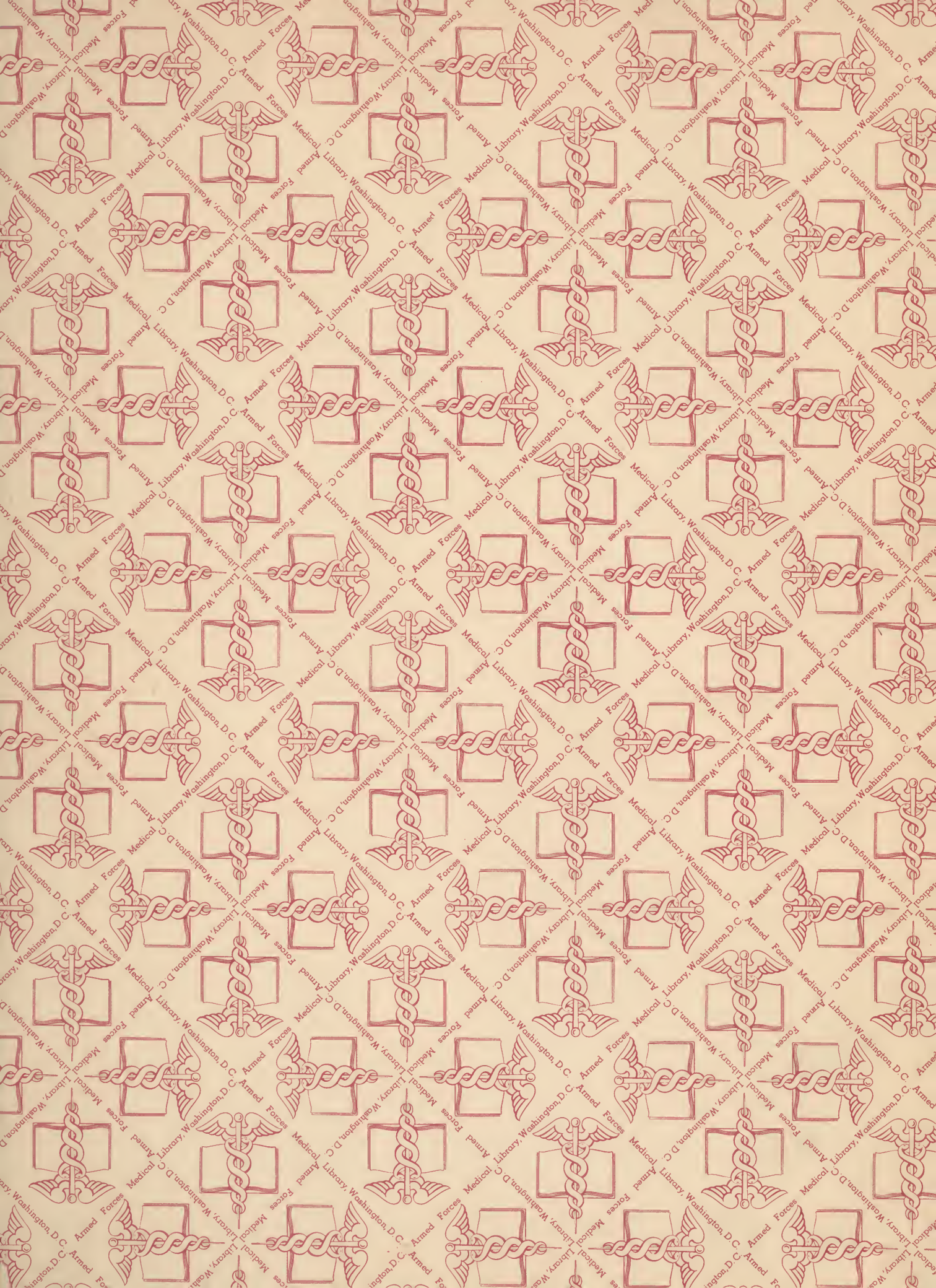
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Section 9-3

Formal Report on "A System for the Ultimate Analysis of Chemical Warfare Agents, Parts I and II"

Service Directive CWS-6

Endorsement (1) from Carl G. Niemann, Division Member in Charge of the Section on Detection and Analytical Problems (9-3) to Walter R. Kirner, Chief, Division 9.

Forwarding report and noting:

> "This report is a system of analysis for the acidic elements likely to be found in chemical warfare agents and is part of a general scheme for the identification of chemical warfare agents. This report can be considered as a final report on one phase of the work done under this contract."

(2) From Dr. W.R. Kirner, Chief, Division 9, to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring.

This is a final report on one phase of the work being done under contract OEMsr-325 (9-256) with California Institute of Technology. Any additional material will be submitted as supplements.

DIVISION 9

NATIONAL DEFENSE RESEARCH COMMITTEE
OF THE
U.S OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Final Report on "A System for the Ultimate Analysis of Chemical Warfare Agents Parts I and II"

to

February 1, 1944

by

E.H. Swift and Carl Niemann

Report O.S.R.D. No. 3693

Copy No. 55

Date: May 29, 1944

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INTRODUCTION

Part I of this report provides procedures for decomposing a sample by a fusion with sodium peroxide in a Parr Micro or Semi-Micro Bomb, and for obtaining a solution and a residue from the fusion melt. Part II provides a system of analysis for certain acidic elements. Part III (not included in this report) provides a system of analysis for certain basic elements.

This report is a complete revision of Part I of Informal Report No. 56, "A System for the Ultimate Analysis of Chemical Warfare Agents", Section 9-2-1, submitted in January, 1943. Revisions and extensions of parts of Part I of Informal Report No. 56 have been issued from time to time; this present report is to replace those revisions and extensions as well as the original Part I.

Part II of Informal Report No. 56 was replaced by Informal Report No. 78, Section 9-3, submitted in June, 1943.

The present report has been divided into Part I and Part II. As a result of this, Informal Report No. 78 now becomes Part III of "A System for the Ultimate Analysis of Chemical Warfare Agents".

An appendix which is a collective appendix for Parts I, II, and III (i.e., for the procedures in this report and for those in Informal Report No. 78) is being issued as a separate informal report. The appendix contains a complete list of reagents, with methods of preparation and amounts necessary for an analysis, and of the apparatus required, and of techniques used.

To summarize: Parts I and II are contained in this report. Informal Report No. 78 is now Part III. The appendix is being issued (March, 1944) in an informal report.

A procedure for handling samples with boiling points between -30 °C and 40° C and for sealing these samples in glass capsules suitable for analysis will be described in a supplement to "The Separation and Purification of Decigram Quantities of Warfare Agents", Informal Report No. 83.

In both Parts II and III, systematic group separations have been used as the first steps in the analysis.

The interferences in the analysis for the acidic elements caused by the basic elements analyzed for in Part III have been investigated. In general, either the interferences have been eliminated by modifications of the procedures or the interferences have been mentioned in the notes to the procedures.

Alternative procedures for the determination of carbon are provided: a dry combustion method and a wet combustion method.

In numbering the procedures each group is assigned a Roman number; procedures within the groups carry the group number followed by consecutive Arabic numbers. Roman numbers below eleven are reserved for the analysis of the acidic elements; eleven and numbers above eleven designate the analysis for the basic elements. The supplementary qualitative procedures for the specific detection of certain elements are indicated by adding a letter to the group procedure number.

Acknowledgment

The general features of this system of analysis for the acidic elements were developed in preliminary form in collaboration with Dr. Clark Gould Jr. The subsequent work has been carried out as a cooperative project to such an extent that it is difficult to properly acknowledge the specific contributions made by individuals. Those who have been responsible for certain procedures, for general changes and improvements, or who have made valuable suggestions include Edward Bennet, Anthony Briglio, David Brown, Paul Farrington, Franklin Hepner, George Holzman, Thomas Lee, John Sease, and James Wendell. Thomas Lee has been largely responsible for the final revision and for the preparation of this report.

Most of the analytical methods used in this system have been taken from well-known standard reference works or from the original literature.

ABSTRACT

The purpose of this report is to provide procedures for the detection and estimation of the acidic elements which may occur in chemical warfare agents. These procedures are part of a system of analysis for both acidic and basic elements in chemical warfare agents. The general features of the procedures of this report are outlined below.

Elements Provided For

In this report, procedures are provided for:

(1) the systematic detection and semi-quantitative determination, by volumetric or colorimetric methods, of arsenic, boron, bromine, chlorine, chromium, fluorine, iodine, phosphorus, selenium, silicon, sulfur, and tellurium.

(2) the quantitative determination of nitrogen.

(3) the quantitative determination of carbon and hydrogen.

Nature of Sample

These procedures are designed for the analysis of toxic warfare agents. They are applicable to most organic compounds and to most inorganic compounds which are not of a resistant nature. The procedures are independent of, and give no indication as to the oxidation states of the elements in the sample. The sample can be a solid or it can be a liquid with a boiling point higher than 40° C. The sample can also be a liquid or gas with a boiling point below 40° C provided that it is sealed in an appropriate glass capsule (see Introduction).

Technique

The procedures employ techniques commonly used in semi-micro analysis, qualitative and quantitative.

Size of Sample

The amounts of sample needed are:

(1) 10-20 mg for the detection and estimation of those elements provided for by the systematic analysis.

(2) 15-30 mg for the determination of nitrogen.

(3) 15-25 mg for the determination of carbon and hydrogen by the dry combustion method or 10-12 mg for the determination of carbon by the wet method.

Sensitivity of Detections

The sensitivity of the detection of those elements provided for in the systematic analysis is 1% of the sample; that is, any of the elements mentioned above which constitutes as much as 1% of the original sample should be detected.

Accuracy of Estimations

The accuracy of the estimation of those elements provided for in the systematic analysis is ± 0.3 mg in a 10-20 mg sample; that is, the amount of the element present can be estimated to within a deviation of ± 0.3 mg. However, deviations of as much as ± 0.8 mg may occur with certain combinations of elements present in large quantities.

The accuracy of the determination of nitrogen is ± 0.1 mg.

The accuracy of the determination of carbon by the dry combustion method is ± 0.05 mg.

The accuracy of the determination of carbon by the wet method is ± 0.05 mg.

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Part I

FUSION OF THE SAMPLE

Part II

THE SYSTEM OF ANALYSIS FOR THE ACIDIC ELEMENTS

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FUSION OF THE SAMPLE

Tabular Outline I

The Behavior of the Elements in the Sodium Peroxide Fusion*

F. I. Fuse the sample with Na_2O_2 and sucrose in a Parr micro or semi-micro bomb. Dissolve the melt. Boil until peroxide is decomposed. Add $N_2H_4.H_2O$. Boil. (IO_3^- and IO_4^- reduced to I^-)

Add H_2O_2. Boil until peroxide is decomposed. (Excess N_2H_4 oxidized to N_2)

Centrifuge. Dilute the centrifugate to an exact volume.

The Fusion Solution	The Fusion Residue
Acidic Elements**	Non-Amphoteric Basic Elements
I^-, Br^-, Cl^- (the Halogen Group)	Fe_2O_3, TiO_2, MnO_2 (the Iron Group)
$CrO_4^=$, $H_4TeO_6^=$, $AsO_4^=$, $PO_4^=$ (Arsenic Group)	$Ni(OH)_2$, $Cd(OH)_2$ (the Cadmium Group)
$SeO_4^=$, $SO_4^=$ (the Sulfur Group Elements)	$Mg(OH)_2$, $BaCO_3$, $SrCO_3$, $CaCO_3$ (the Alkaline Earth Group)
$H_2BO_3^-$	SnO_2, $Na_2H_4TeO_6$, $NaSb(OH)_6$, CuO, PbO_2 ****
F^-, NO_3^-, $SiO_3^=$	
Amphoteric Basic Elements***	
$SeO_4^=$, $H_4TeO_6^=$ (the Selenium Group)	
$Cu(OH)_4^=$, $Pb(OH)_4^=$, $Cd(OH)_2$, $Zn(OH_4)^=$ $AsO_4^=$, $Sb(OH)_6^-$, $Sn(OH)_6^=$ (the Hydrogen Sulfide Group)	

* The estimations of nitrogen and of carbon and hydrogen are made on separate portions of the original sample (see Tabular Outline I-a).

** The analysis for the Acidic Elements is made on several portions of the Fusion Solution. A 10 ml portion is analyzed for I, Br, Cl, Cr, Te, As, P, Se, S, and B. A 2 ml portion is analyzed for F, and a 1 ml portion is analyzed for Si. Furthermore, qualitative tests for I, Br, Te and Se, As, P, and N are made on separate portions of the solution.

***The analysis for the Amphoteric Basic Elements is made on a single 10 ml portion of the Fusion Solution. The analysis for the Non-Amphoteric Basic Elements is made on the Fusion Residue.

****These elements are present here only when occuring in large amounts.

FUSION OF THE SAMPLE

P. I-A
P. I-B

The Fusion of the Sample and Solution of the Fusion Mixture

Procedure I has been divided into two sections in order to secure greater clarity of presentation. The first section, P. I-A, contains the procedure for fusing the sample in the nickel bomb. P. I-B contains the procedure for dissolving the soluble components of the mixture resulting from the fusion and for the separation from the solution of the insoluble components. This residue and the solution will hereafter be designated the Fusion Residue and Fusion Solution respectively.

P. I-A

Fusion of the Sample

Alternative fusion procedures are given. It is recommended that the semi-micro bomb be used (a) if an analysis for both Acidic and Basic Elements is desired or (b) if an analysis for the Acidic Elements is desired and an adequate amount of sample is available. The micro bomb should be used (a) if an analysis for only the Acidic Elements is desired and the amount of sample is limited or (b) if an analysis for only the Basic Elements is desired. Note 1 contains a discussion of the amounts of Fusion Solution needed for the various analyses.

Option 1. In case the sample is to be fused in a semi-micro bomb, fit the fusion cup of a nickel Parr semi-micro bomb (Note 2) with its protecting bomb body (see Fig. 1). Place the assembly in a 50 ml beaker and flush it and the beaker with a stream of oxygen or, if oxygen is not available, with carbon dioxide (Note 3). If the sample to be analyzed is a solid or high boiling liquid (Note 4), add 90-100 mg of finely ground dry sucrose (Note 5) to the fusion cup. Add 20-40 mg of the sample (Note 6) so that it is all either absorbed by or rests on the sucrose. Again add 90-100 mg of sucrose; take care to cover the sample completely (Note 7). Add 4 g of Na_2O_2 (Note 8) and brush any excess sodium peroxide from the lip of the bomb (Note 9). Close the fusion cup with the bomb cover and the screw cap. Place the assembly in the bench socket and tighten the screw cap with the Parr wrench; a

Fusion cup with cover

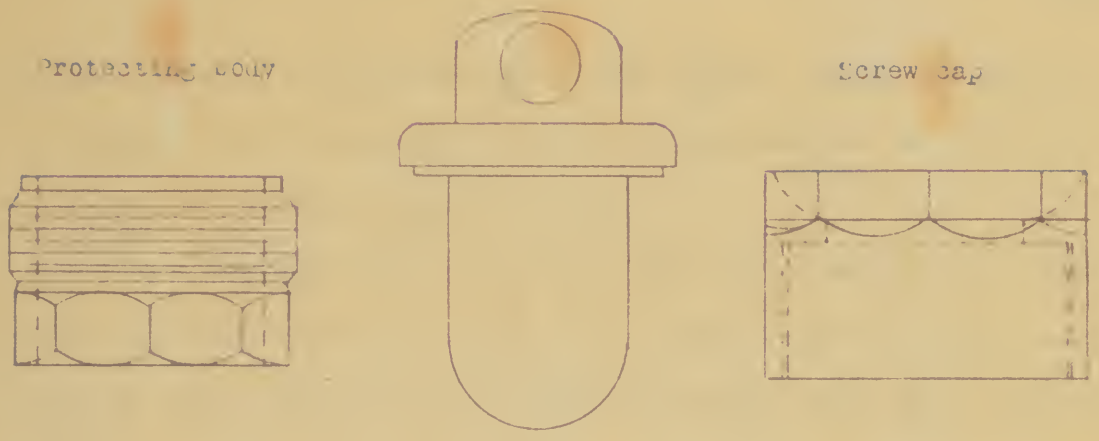

Figure 1. Parr Semi-Micro Bomb and Protecting Body

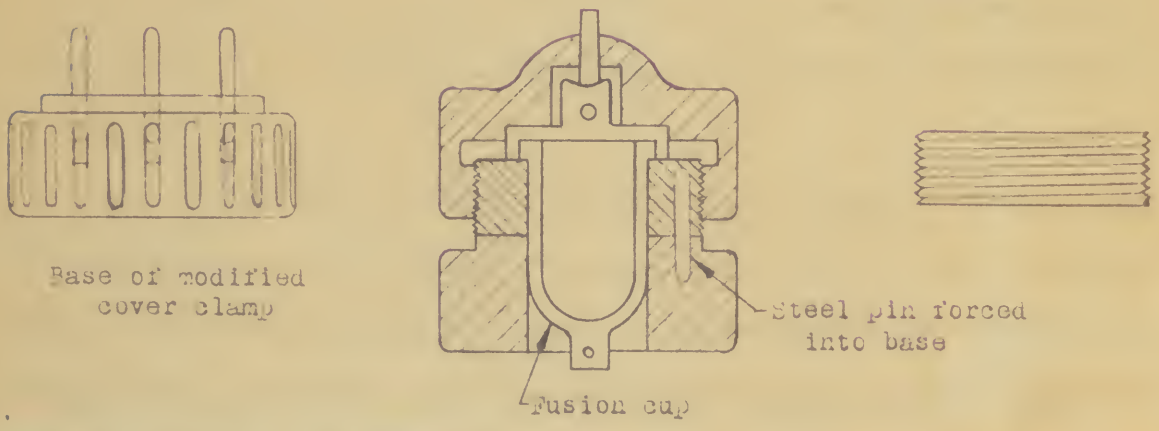

Figure 2. Parr Micro Bomb and Modified Cover Clamp

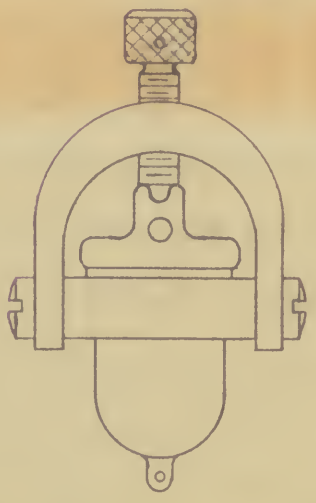

Figure 3. Parr Micro Bomb and Parr Yoke

strong pull should be exerted on the wrench handle. Shake the closed bomb violently for 30 seconds; then tap the bomb sharply on a board in order to pack the contents into the bottom.

Heat the lower part of the bomb (Note 10) with the hot non-luminous tip of a Bunsen burner flame until a slight "bump" or hissing sound is noticed; then heat for an additional 30 seconds (Note 11). Cool the bomb under a stream of water and finally rinse it with distilled water. Treat the bomb and its contents by P. I-B below.

If an analysis for the Acidic Elements is to be made, prepare a blank fusion in a semi-micro bomb (Note 12) by taking the amounts of sucrose and Na_2O_2 specified above. Treat the bomb and its contents by P. I-B.

Option 2. In case the sample is to be fused in a micro bomb, fit the fusion cup of a nickel Parr micro bomb (Note 2) with the modified cover clamp and base or with the Parr yoke and bench socket (Note 13 and Figs. 2 and 3). Place the assemble in a small beaker and flush it and the beaker with a stream of oxygen or, if oxygen is not available, with carbon dioxide (Note 3). If the sample to be analyzed is a solid or high boiling liquid (Note 4), add 40-50 mg of finely ground dry sucrose to the fusion cup (Note 5). Add 10-20 mg of the sample (Notes 14 and 6) so that it is all either absorbed by or rests on the sucrose. Again add 40-50 mg of sucrose; take care to cover the sample completely (Note 7). Add 2 g of Na_2O_2 (Note 8) and brush off any excess sodium peroxide from the lip of the bomb (Note 9). Close the bomb and clamp the cover tightly in place by hand (if the modified cover clamp is used) or with the aid of the pin wrench (if the Parr yoke is used). Shake the closed bomb violently for 30 seconds; then tap the bomb sharply on a board in order to pack the contents into the bottom. If the modified cover clamp and

base are being used, remove the base.

Holding the bomb at an angle, heat the lower part of the bomb (Note 10) with the hot non-luminous tip of a Bunsen burner flame until a slight "bump" or hissing sound is noticed; then heat for an additional 20 seconds (Note 11). Cool the bomb under a stream of water and finally rinse it with distilled water. Treat the bomb and its contents by P. I-B.

If an analysis for the Acidic Elements is to be made, prepare a blank Fusion Solution in a semi-micro bomb as described in the last paragraph of Option 1 above (Note 12).

Notes.

1. A fusion in a micro bomb gives 25 ml of Fusion Solution; the semi-micro bomb gives 50 ml. An analysis for all of the Acidic Elements (I, Br, Cl, Cr, Te, As, P, Se, S, B, F, Si, N) requires 23 ml of Fusion Solution; 13 ml are required for the quantitative analysis and 10 ml for various qualitative tests. (However, when Halogen Group Elements and Arsenic Group Elements are absent, only 22 ml are required.) When making a complete analysis for the Acidic Elements it is better to use a semi-micro bomb because of (a) the necessary losses in transferring aliquots of the Fusion Solution, (b) the possibility that a confirmatory test for boron might be helpful, (c) the possibility that another, smaller aliquot of Fusion Solution should be analyzed for fluorine (see Note 4, P. VI), (d) the possibility that some tests (especially qualitative tests) have to be repeated.

However, the analysis for the Acidic Elements requires only 20 ml if the qualitative test for nitrogen is made on a 1 mg portion of the original sample by the procedure provided in the "Qualitative Tests for Certain Acidic Elements in Organic Compounds", Informal Report No. 85, or if the qualitative test for nitrogen is omitted and only a quantitative estimation is made by P. VII. Further, the omission of the detection and estimation of fluorine saves 2 ml of Fusion Solution, the omission of that for silicon saves 1 ml.

The complete analysis for the Basic Elements (Fe, Ti, Mn, Ni, Cd, Mg, Ba, Sr, Ca, Se, Te, Cu, Pb, Zn, As, Sb, Sn, Cr) requires 10 ml of the Fusion Solution.

2. Bombs made of "Illium" are not satisfactory; with such bombs significant amounts of chromium are found in the fusion mixture.

3. If the nitrogen of the air is not removed before fusion, 20-80 gamma of nitrogen are introduced into the Fusion Solution from this source. Oxygen is conveniently obtained from a tank or generator. If a detection of nitrogen is not of interest, the air need not be flushed from the fusion cup with oxygen or carbon dioxide.

4. A sample which boils below 40° C. cannot be handled by the pycnometer technique (see Note 6) and, prior to analysis, must be sealed in a glass capsule as described in the Supplement to Informal Report No. 83. In this case, prepare the fusion mixture in the fusion cup as follows:

> Add to the fusion cup, which has been flushed free of air, 180-200 mg of sucrose (if the semi-micro bomb is used) or 80-100 mg (if the micro bomb is used). Add 4 g of Na_2O_2 (if the semi-micro bomb is used) or 2 g (if the micro bomb is used) and brush off any excess from the lip of the fusion cup. Close the fusion cup with the bomb cover and shake the

closed bomb violently for 30 seconds; then tap the bomb sharply on a board in order to pack the contents into the bomb bottom. Remove the bomb cover and bury the glass capsule in the fusion charge; (that part of the glass capsule which contains most of the sample should be at the bottom of the bomb). Close the bomb and clamp the cover in place. Then heat the fusion charge as directed.

5. The sucrose should bd perfectly dry; otherwise it may react with the Na_2O_2 on contact. The sucrose should be of the purest obtainable grade. Figure 4 shows convenient cups for measuring sucrose and Na_2O_2. A convenient

Figure 4. Glass Measuring Cup
For the sucrose a 20 mm length of 7 mm glass tubing fastened to a 160 mm length of 5 mm glass rod is a convenient size. Check the weight of sucrose delivered and make a calibration mark if necessary.
A 40 mm length of 10 mm glass tubing with handle as above may be calibrated to deliver 2 g of Na_2O_2

measuring cup for the Na_2O_2 is made by the Parr Instrument Company. The measuring dipper is calibrated to deliver 4 g ($\pm$ 0.1 g) of Na_2O_2.

6. It is assumed that the analyst is familiar with the precautions to be taken in handling toxic materials, especially with the necessity of working in well ventilated hoods and wearing protective gloves (and mask if necessary) and with the most effective means of decontaminating his person and equipment (see Appendix I, "A Separation and Purification of Decigram Quantities of Warfare Agents", Informal Report No. 83).

The following parts of this note concern weighing the sample. Remember that when glass capsules are used to contain the sample during fusion, silicon, calcium, and boron are introduced into the Fusion mixture.

A. Solids can be conveniently handled in weighing tubes (see Fig. 5).

Figure 5. Weighing Tube
Handle 130 x 2 mm; tube 20 mm long with outside diameter not less than 5 mm; ground glass fitted cap.

B. Liquids with boiling points above 80° C. can be handled by means of the pycnometer (see Fig. 6), which, when calibrated with distilled water, is also convenient for determining the densities of the liquids. (For more detailed information about the use of the pycnometer, see P. II-3, Informal Report No. 83.)

Figure 6. Pycnometer (actual size)

The pycnometer is made from 0.5 mm bore Pyrex tubing by drawing out both ends and then sealing to one end a short length of 6-7 mm O.D. Pyrex tubing. The caps are made from 6-7 mm Pyrex by drawing out one end (so as to leave an air vent hole) and by flaring the other end to fit the pycnometer. The joints can be ground with corundum powder so that they fit tightly. This pycnometer holds 10 microliters of liquid. If the sample is to be fused in a semi-micro bomb, either use two portions of sample from this pycnometer or construct a longer one.

In case the density of the liquid is to be taken, treat the sample by P. II-3 of Informal Report No. 83. Then extrude the sample into the bomb and weigh the empty pycnometer as described below.

Clean a pycnometer by washing it successively with carbon tetrachloride, ethyl alcohol, and distilled water. Flush the capillary tube with the cleaning solvent by drawing the liquids upwards with the aid of a rubber nipple connected to the pycnometer (see Fig. 7). Dry the pycnometer parts in an oven and let them cool to room temperature. Assemble the parts and wipe the exterior of the tube with moistened chamois skin (see Note 2, P. II-3, Informal Report No. 83). Place the pycnometer on the pan of an analytical balance, and let it stand for 5 minutes; then weigh it to within 0.05 mg.

Attach the rubber nipple and the glass tubing containing the air vent to the pycnometer (see Fig. 7). Squeeze the rubber nipple, then place a forefinger

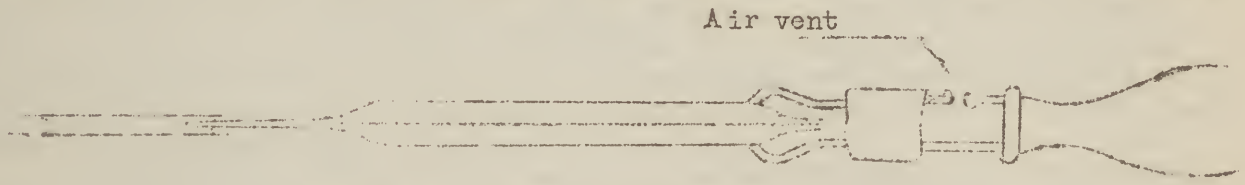

Figure 7. Filling the Pycnometer

over the vent. Insert the tip of the pycnometer into a 15-25 mm column of liquid contained in a 2 mm capillary tube (see Note 4, P. II-3, Informal Report No. 83) and, holding the pycnometer horizontally, allow the liquid to be drawn into the pycnometer until it fills an appropriate portion of the bore (for the micro bomb, a 10-20 mg sample is wanted; for the semi-micro bomb, 20-40 mg); then remove the finger from the air vent. Wipe off the outside of the wet tip with absorbent paper, place the glass caps on the pycnometer and weigh it.

Fit the rubber nipple and glass tubing to the pycnometer. With a finger closing the vent, carefully extrude the liquid into the bomb. Place the glass caps on the pycnometer. Do not wipe the tip of the pycnometer free of liquid. Put the pycnometer on a balance, allow it to stand 3-4 minutes, and weigh it.

C. Liquids with boiling points above 40° can be handled conveniently by means of a Pregl capsule. In this method the liquid sample is drawn up into a warmed glass capsule (see Fig. 8).

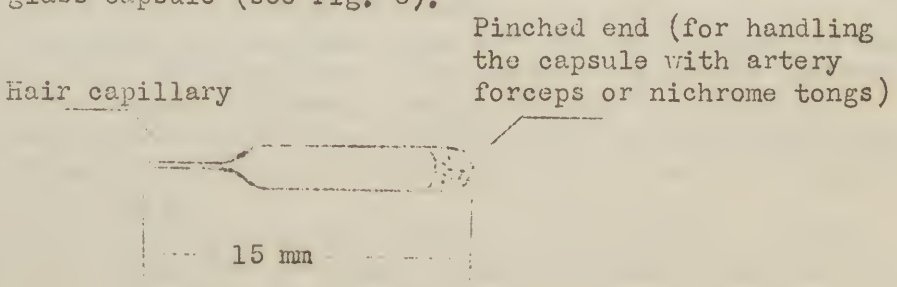

Figure 8. Pregl Glass Capsule

Made from 2 mm O.D. capillary tubing drawn from 20 mm O.D. standard wall soft glass tubing.

The procedure is as follows:

Heat the glass capsule by holding it in constant motion about 3 cm above the tip of a non-luminous microburner flame for 5-10 seconds (nichrome tongs or artery forceps (serrafins) are convenient for holding the capsule). Take care not to heat directly the hair capillary of the capsule. Cool and weigh the empty capsule. Heat the capsule again as above and then submerge the tip beneath the surface of the liquid sample for 10-30 seconds (depending on the amount of sample desired). Withdraw the capsule from the liquid, wipe the outside of the tip with absorbent paper, and weigh again.

D. Liquids with boiling points below 40° C. must be condensed into small glass capsules by the method described in Informal Report No. 83.

7. Any of the sample on the sides of the bomb or not covered completely by the sucrose may react with the Na_2O_2 before the bomb is closed.

8. As this system of analysis is designed to detect the various constituents in amounts as small as a few micro-grams (hereafter designated as gamma), it is imperative that only the highest grade of chemicals be employed. Even when this is done it is absolutely necessary that the blanks (provided by the following procedures in this system) be made before deciding as to the presence of small amounts of various constituents. These blank tests are made on the blank fusion solution. The preparation of this solution is described in the last paragraph of this procedure.

If available, "Baker's C.P. Analyzed Sodium Peroxide, Calorific Grade, Special, Low in S and SiO_2" should be used. Other grades of Na_2O_2 contain such considerable amounts of chlorine, sulfur, and silicon that the detection of small quantities of these elements in the original sample is difficult.

In case the sample may contain tin and a precise analysis for this element is desired, add 0.20 g (in case the micro bomb is used) or 0.40 g (in case the semi-micro bomb is used) of finely powdered, dry NaOH (Baker's Special Stick NaOH, Low in CO_2, Cl, PO_4, and Fe) to the fusion charge. If this NaOH is not available, no other (less pure) grade should be substituted. The presence of NaOH in the fusion charge has been found to diminish greatly the fraction of any tin which may be present which is converted to refractory SnO_2 during the fusion, and, hence, to diminish the fraction of the tin which will be present in the Fusion Residue.

9. Any Na_2O_2 on the lip of the bomb will come in contact with the lead gasket and will attack it vigorously during the combustion. After 5-10 fusions, the lead gaskets become pitted and should be replaced. Lead gaskets may vary in hardness; therefore, a cover with a new gasket should be tested by a blank fusion to see that it makes a firm seal with the bomb.

10. Because the gasket may be blown out, heat the bomb behind an explosion shield. Heat only the protruding tip of the micro bomb or the exposed hemispherical portion of the semi-micro bomb. The micro bomb is conveniently held while heating by grasping the tip of the modified cover or clamp yoke with a pair of tongs; the semi-micro bomb can be held by applying a pair of tongs to the lifting hole in the bomb cover.

11. Sometimes the "bump" or hissing sound is not noticed; in such cases the total heating time should not be longer than 60 seconds with the micro bomb or 90 seconds with the semi-micro bomb; otherwise the lead gasket may be softened.

If the lid is difficult to remove because the gasket adheres to the bomb, apply leverage by means of a metal bar (the handle end of a file may be

used) inserted in the hole provided in the cover.

Gaskets are occasionally blown out. This can be due to peroxide on the lip of the bomb, to a new gasket which does not fit the bomb closely, or to Na_2O_2 which has adsorbed moisture. It has been found that gaskets in the semi-micro bomb are blown out less often than those in the micro bomb, probably because the semi-micro bomb cover can be screwed on more tightly. If a gasket is blown out, replace it, press a ridge into it by screwing the cover onto the bomb as tightly as possible, and make a blank fusion in the bomb. If the gaskets of the micro bomb are blown out repeatedly, fuse the sample in the semi-micro bomb, using micro bomb portions of sample and reagents if desired.

12. The amount of blank fusion solution used in the complete analysis for the Acidic Elements varies from 25 to 35 ml, depending upon whether or not certain elements are present in a sample. No provision is made for blank tests in the Analysis for the Basic Elements, but such tests might be useful.

13. If available, the modified cover clamp should be used.

14. In general, the combustion of the material in the micro bomb will be more complete if the sample is limited to 10-15 mg. A 15-20 mg sample should be taken when the primary interest is in the qualitative detection of the minor constituents of a mixture.

P. I-B Solution of the Fusion Mixture

Open the bomb and wash the cover with 35-45 ml of water (in case the semi-micro bomb was used in P. I-A) or 25-30 ml of water (in case the micro bomb was used in P. I-A); collect the water in a 125 ml platinum evaporating dish (Notes 15 and 16).

Place the bomb in the dish, cover with a watch glass, and heat carefully in the oxidizing flame of a Bunsen burner until oxygen is steadily evolved (Note 17). The platinum dish can be conveniently supported by placing it on a section of "transite" board which has a hole somewhat smaller than the largest diameter of the platinum dish and which is placed on or fastened to an iron ring (see Fig. 9). The heating should be cautiously continued until the "melt" is completely dissolved from the bomb (as shown by absence of bubble formation on the inner surface). Remove the bomb, while washing it with a fine jet of water. When the evolution of oxygen has stopped, as shown by the absence of small bubbles (usually after 3-5 minutes of boiling), remove the flame and cool the platinum dish and its contents to room temperature. While stirring the mixture, pipet into it 0.20 ml of 85% $N_2H_4.H_2O$ (if the semi-micro bomb was used) or 0.10 ml of 85% $N_2H_4.H_2O$ (if the micro bomb was used) (Note 18). Remove the watch glass cover, boil the solution 3 minutes. Cool the mixture to room temperature and replace the watch glass

(Note 19). Add 6 ml of phosphate-free 30% H_2O_2 (if the semi-micro bomb was used) or 3 ml of phosphate-free 30% H_2O_2 (if the micro bomb was used) (Notes 20 and 21). Carefully heat the mixture until it boils, then evaporate it to approximately 25 ml (if the semi-micro bomb was used) or 15 ml (if the micro bomb was used) (Note 22).

Transfer the mixture to a 30 ml graduated centrifuge tube (Note 23); rinse any residue from the dish with two 1 ml portions of hot water. Cool the mixture to room temperature and centrifuge it until the solution is clear. (Residue: probable presence of certain metallic oxides, hydroxides, or carbonates. Note 24.) Reserve the platinum dish for treatment by P. XI.

In case the centrifugate is turbid (Note 25), filter the centrifugate through a hardened filter paper (as Whatman No. 50) (Note 26); finally collect the filtrate in a 50 ml volumetric flask (if the semi-micro bomb was used) or in a 25 ml flask (if the micro bomb was used) (Note 27). Wash the filter paper with two 1 ml portions of water, collecting the washings in the platinum dish. Reserve the filter for treatment by P. XI. Swirl the wash water in the platinum dish and pour the solution into the centrifuge tube containing the Fusion Residue. Reserve the platinum dish for treatment by P. XI. Stir the Residue thoroughly with the wash water. Centrifuge the mixture and add the centrifugate by means of a dropper to the Fusion Solution in the volumetric flask.

In case the centrifugate is clear (Notes 24 and 25), pour the centrifugate, with the aid of a stirring rod (see Operation 3, Appendix V), to a 50 ml volumetric flask (if the semi-micro bomb was used) or into a 25 ml volumetric flask (if the micro bomb was used). Wash the Fusion Residue and the centrifuge tube with two 1 ml portions of water; (see Operations 2 and 1, Appendix V); collect the washings with the main centrifugate (Note 27).

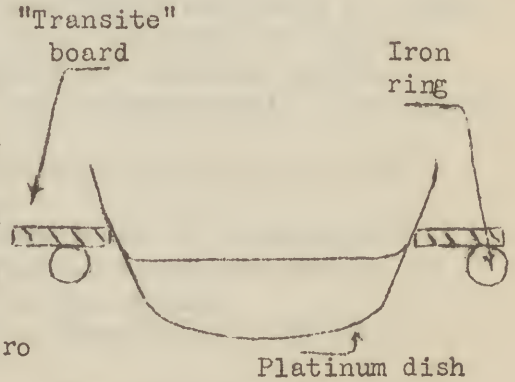

Figure 9. Support for Platinum Dish

Dilute the solution in the volumetric flask to the calibration mark.

In case it is desired to perform the Analysis for the Basic Elements (Note 28), immediately pipet 10 ml of the Fusion Solution into a specially calibrated (see Note 1, P. XVIII) 50 ml conical flask, stopper the flask and reserve it for treatment by P. XVIII; reserve the Fusion Residue for treatment by P. XI.

Analyze the Fusion Solution for the Acidic Elements as directed in P. II.

Notes.

15. The bomb cover should not be heated with the alkaline solution of fusion mixture since the lead of the gasket is attacked by this solution.

The Fusion Solution is evaporated in a platinum dish, rather than in a beaker, because silica and boron are dissolved when alkaline solutions are boiled in Pyrex vessels. If a platinum dish is not available, a new, unscratched Pyrex beaker may be used if the evaporation is not prolonged. With unscratched glassware, usually less than 50 gamma of boron are dissolved.

16. If the solid "melt" is green, manganese (as manganate) is probably present.

A good combustion is characterized by no carbon residue or only a very small amount. If the Fusion Solution contains a large amount of carbon residue, it is advisable, if more sample is available, to repeat the fusion using one-half the amount of sucrose suggested in the procedure.

Certain elements, when present in significant amounts, will produce a color in the Fusion Solution. For example, copper yields a blue solution and chromium a yellow solution. (Also vanadium will color the Fusion Solution yellow.)

Fusions of various toxics (with and without the glass capsules) have resulted in solutions which have had a gray, yellow, orange, or purple color. Often the color remains after the precipitation of any Halogen Group elements in P. II. In some cases a slow precipitation of the material may occur in the acid centrifugate from the Halogen Group precipitate when this solution stands, or upon neutralization of this solution preparatory to the Arsenic Group precipitation (P. III). These effects may be due to finely suspended carbon, silicic acid, silica, or to the coagulation of certain metallic oxides.

17. The "melt" should be leached from the bomb and the solution boiled carefully at first in order to avoid loss of solution by rapid evolution of oxygen.

18. Hydrazine is added to reduce any iodate or periodate to iodide. Copper, if present, will be reduced from $Cu(OH)_4^=$ to Cu_2O or metallic copper; chromate will be partiall reduced to chromic ion; and tellurate will be partially reduced to tellurium metal.

19. If the cover glass is not removed, hydrazine distills from the solution and condenses on the glass.

If the mixture is warm, the H_2O_2 subsequently added may decompose so rapidly that it does not oxidize all of the N_2H_4. The decomposition of H_2O_2 is especially rapid when copper or chromium is present in the sample.

20. Use either "Merck Reagent Superoxol" or Baker's "C.P. Special 30% Hydrogen Peroxide".

If these reagents are not available, Baker's "C.P. Hydrogen Peroxide" or Merck's "C.P. Superoxol" can be used. In this case remember that amounts of phosphate and sulfate capable of interfering with the detection of phosphorus and sulfur may be introduced (see Note 3, P. III-8 and Note 2, P. IV-2).

If all of these reagents are unavailable, do not use an inferior grade of H_2O_2 but substitute solid Na_2O_2. In this case, add 4 g of Na_2O_2 (if the

semi-micro bomb was used) or 2 g (if the micro bomb was used). The use of Na_2O_2 is to be avoided when possible, as it gives a Fusion Solution which is 4 F in NaOH instead of 2 F as usual.

21. Hydrogen peroxide is added in order to destroy excess hydrazine. Metallic copper of Cu_2O will be partially re-oxidized to $Cu(OH)_4^=$. Chromic ion will be oxidized to chromate and metallic tellurium will be oxidized to tellurate.

22. In order to prevent the solution from bumping, heat the platinum dish around the sides with a soft oxidizing flame; do not heat the bottom of the dish for extended periods of time.

Boil the solution for a minimum of 6-8 minutes in order to decompose all of the peroxide.

23. Wash material spattered on the watch glass into the solution.

If available, 30 ml graduated centrifuge tubes are more convenient than 50 ml graduated centrifuge tubes for containing the fusion mixture and also for certain procedures in the Analysis for the Basic Elements. Fifty ml tubes can be used, however.

24. Elements which may be present behave as follows: iron is quantitatively precipitated as the red-brown hydrous oxide, manganese as the brown or black manganese dioxide, titanium as the white hydrous oxide, nickel as the brown-gray oxide, magnesium as the white hydroxide, calcium, barium, and strontium as the white carbonates, (silver as the black silver metal).

In addition to the elements listed above, the following elements may be constituents of the Fusion Residue: cadmium is largely precipitated as the white hydroxide or as the brownish oxide; tin may be partially precipitated as the white stannic oxide; antimony is partially precipitated as the white sodium antimonate; copper is partially precipitated as the red cuprous oxide, and possibly as metallic copper; tellurium is partly precipitated as the white sodium tellurate; lead may be partially precipitated as the red lead dioxide or may be more extensively coprecipitated by other constituents of the Fusion Residue; (cobalt may be partially precipitated as the brown cobalt oxide).

In case a glass capsule was used to contain the sample in P. I-A, silicon will be partially precipitated as hydrated silica. Furthermore, any calcium from the glass will partially precipitate as white calcium silicate and partially as calcium carbonate. All of the calcium will be present in the Fusion Residue, however.

25. Examine the solution very carefully to note any turbidity. Certain precipitates, for example, cadmium or ferric hydroxide, may give a turbid solution. In such cases the centrifugate should be filtered. It has been found that the combination of filtering and centrifuging will give a clearer solution than the repeated application of either operation alone.

26. In case the solution is filtered, a hardened filter paper (as Whatman No. 50) should be used in order to retain the colloidal hydroxides. The solution is filtered through a conical filter funnel attached by means of a one-hole rubber stopper to a 125 ml flask with side arm (if the semi-micro bomb was used) or a 150 x 18 mm test tube with side arm (if the micro bomb was used; see Fig. 10). Apply suction to facilitate the filtration. The filtrate can be transferred with the aid of a stirring rod (see Operation 3, Appendix V) to the appropriate size volumetric flask.

27. In case the detection and estimation of boron or silicon in the Fusion Solution is of interest, the solution (and the blank fusion solution as well) should be transferred from the volumetric flask, immediately after dilution to the calibration mark, to a paraffined bottle. If this is not done, no significance can be attached to the results of analyses for boron or silicon, as these elements are rapidly dissolved from Pyrex glass by the alkaline Fusion Solution.

28. In case it is desired to analyze for the Basic Elements, a 10 ml aliquot portion of the Fusion Solution is immediately transferred to the 50 ml conical flask used to begin this analysis, since antimony and tellurium, if present,

may slowly precipitate from the Fusion Solution as sodium antimonate and sodium tellurate, respectively.

Figure 10. Filtering Apparatus
Side arm test tube (150 x 18 mm); No. 1 rubber stopper; 45 mm funnel with 50 mm stem.

PART II

THE SYSTEM OF ANALYSIS FOR THE ACIDIC ELEMENTS

Tabular Outline I-A

The Separation of the Acidic Elements into Groups

Solution: I^-, Br^-, Cl^-, $CrO_4^=$, $H_4TeO_6^=$, $AsO_4^=$, $PO_4^=$, $SeO_4^=$, $SO_4^=$, $H_2BO_3^-$, (F^-, $SiO_3^=$, NO_3^-, Amphoteric Basic Elements*), Na^+OH^-, $Na_2^+CO_3^=$,

P. II. Take an aliquot portion. Add $HClO_4$ and $AgNO_3$.

Precipitate:	Solution: $HCr_2O_7^-$, H_6TeO_6, H_3AsO_4, H_3PO_4, $HSeO_4^-$, HSO_4^-, H_3BO_3.			
AgI, AgBr,	P. III. Add more $AgNO_3$. Neutralize to pH 6-7 with Na_2CO_3.			
AgCl.	Precipitate: Ag_2CrO_4,	Solution: $SeO_4^=$, $SO_4^=$, H_3BO_3.		
The Halogen	$Ag_2H_4TeO_6$, Ag_3AsO_4,	P. IV. Add HCl. Centrifuge.		
Group	Ag_3PO_4.	($AgCl$, $HSeO_4^-$, HSO_4^-, H_3BO_3)		
To P. II-1.	The Arsenic Group	Discard AgCl.		
	To P. III-1.	P. IV-1. Add HBr and $NH_2OH.H^+Cl^-$.		
		Precipitate:	Solution: HSO_4^-, H_3BO_3.	
		Se.	P. IV-2. Add NaOH and $BaCl_2$.	
		To P. XVIII-1.	Precipitate:	Solution:
			$BaSO_4$.	H_3BO_3.
			To P. IV-3.	To P. V-1.

* The analyses for F, Si, N, and the Amphoteric Basic Elements are made on separate portions of the Fusion Solution. Provisions are made in the procedures for eliminating all interferences caused by these elements.

Tabular Outline I-a

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Procedure Sequence for the Separation of the Acidic Elements into Groups*

- P. I. Fusion of the Sample and Solution of the Fusion Mixture
- P. II-a. Qualitative Test for Iodine
- P. II. Precipitation of the Halogen Group — (Halogen Group present) — Analysis of the Halogen Group (see Tabular Outline II-a)
- P. III. Precipitation of the Arsenic Group — Analysis of the Arsenic Group (see Tabular Outline III-a and III-b)
- P. IV. Removal of Silver — (Selenium present as shown by qualitative test--see Tabular Outline III-a) — Estimation of Selenium (see Tabular Outline IV-a)
- P. IV-2. Detection and Separation of Sulfur — (Sulfur present) — Estimation of Sulfur (see Tabular Outline IV-a)
- P. V. Detection and Estimation of Boron — (Boron present) — P. V-a. Confirmatory Test for Boron
- P. VI. Detection and Estimation of Fluorine
- P. VII-a. Qualitative test for Nitrogen — (Nitrogen present) — **P. VII. Quantitative Estimation of Nitrogen
- P. VIII. Detection and Estimation of Silicon

**P. IX. Quantitative Estimation of Carbon and Hydrogen
or
**P. X. Quantitative Estimation of Carbon, Wet Method

* This outline shows only the sequence of the procedures (which is not completely shown by Tabular Outlines I and I-A). This outline does not, in general, indicate the source of the solution analyzed; for example, the solution analyzed by P. II does not come from P. II-a.

**Separate portions of the original sample are used for these estimations.

Tabular Outline II

The Analysis of the Halogen Group

Precipitate from P. II: AgI, AgBr, AgCl.

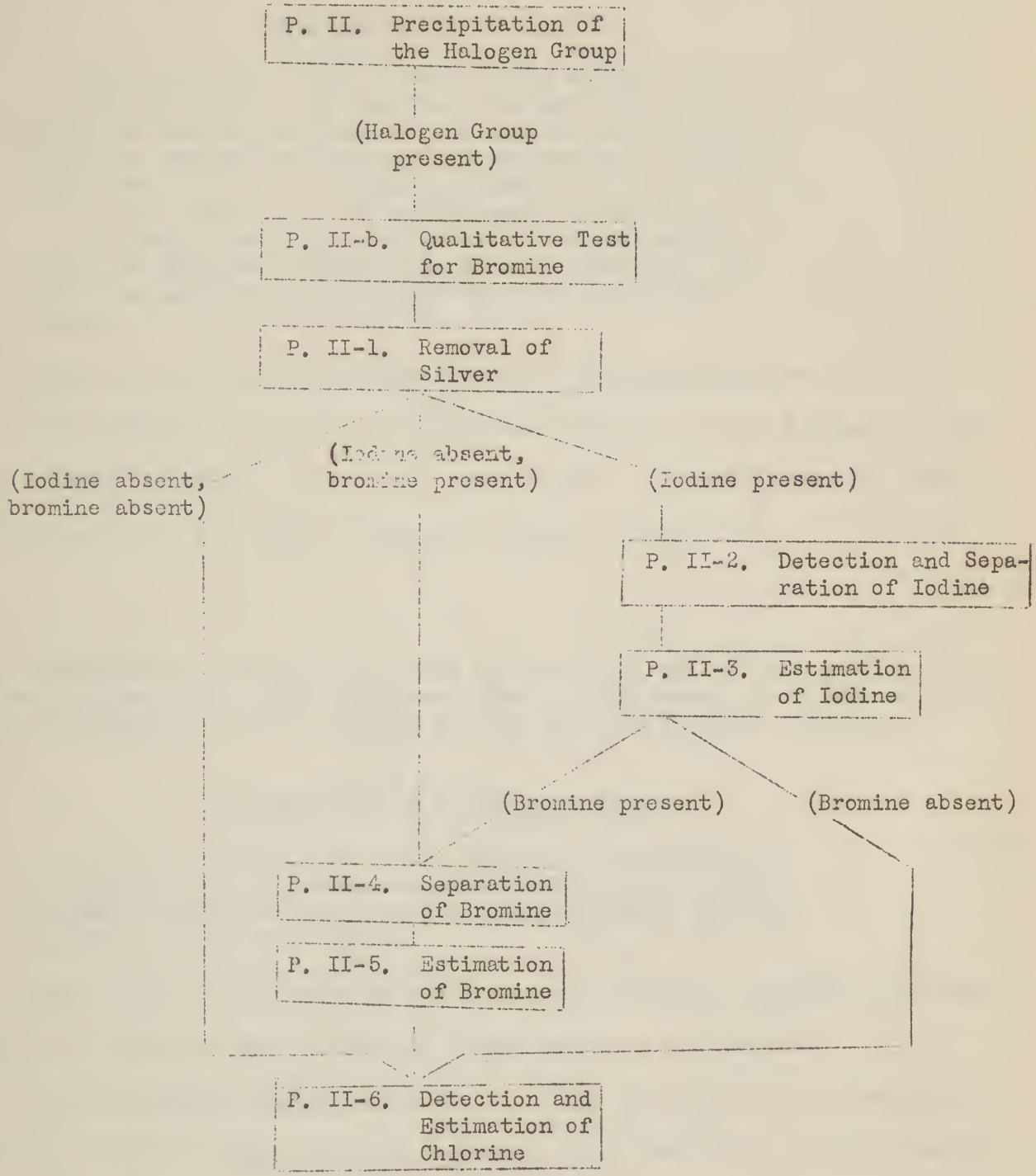
P. II-1. Add NH_4OH, NaOH, and amalgamated zinc. Stir. Add NH_4OH and mercury. Shake.

Residue: Ag and Zn amalgam Discard.	Solution: I^-, Br^-, Cl^-, $Zn(NH_3)_4^{++}$, Na^+OH^-, NH_4OH. Heat to expel most of the NH_3. Acidify with $HClO_4$. P. II-2. Add CCl_4 and $NaNO_2$. Shake.

CCl_4 Layer: I_2. P. II-3. Add KI H_2O, and $HC_2H_3O_2$. (I_3^-) Titrate with $Na_2S_2O_3$. (I^-, $S_4O_6^=$)	Aqueous Layer: Br^-, Cl^-, Zn^{++}, HNO_2, $H^+ClO_4^-$. P. II-4. Boil out NO and NO_2. Add CCl_4 and $KMnO_4$. Shake.	
	CCl_4 Layer: Br_2. P. II-5. Add KI, H_2O, and $HC_2H_3O_2$. (I_3^-, Br^-) Titrate with $Na_2S_2O_3$. (I^-, $S_4O_6^=$)	Aqueous Layer: Cl^-, Mn^{++}, MnO_4^-, MnO_2, Zn^{++}, $H^+ClO_4^-$. P. II-6. Add H_2O_2. (Cl^-, Mn^{++}, Zn^{++}, $H^+ClO_4^-$) Adjust acidity. Add diphenyl carbazone indicator. Add 0.04 ml of 0.015 F $Hg(NO_3)_2$. (Cl^-, unionized $HgCl_2$, diphenyl carbazone, Mn^{++}, Zn^{++}, $H^+ClO_4^-$) Titrate with $Hg(NO_3)_2$ to the appearance of a violet color. (unionized $HgCl_2$, mercury diphenyl carbazone (violet colored), Mn^{++}, Zn^{++}, $H^+ClO_4^-$)

Tabular Outline II-a

Procedure Sequence for the Analysis of the Halogen Group*



* P. II-a, the Qualitative Test for Iodine, is performed before the precipitation of the Halogen Group (see Tabular Outline I-a).

THE ANALYSIS OF THE HALOGEN GROUP

(I, Br, Cl)

P. II-a Qualitative Test for Iodine

This qualitative test is made upon a small portion of the Fusion Solution. It must be performed before P. II is performed because knowledge of the presence or absence of iodine is necessary before the correct option in that procedure can be chosen. Further, if iodine is absent, P. II-2 and P. II-3 can be omitted (see Tabular Outline II-a).

The test depends upon the formation of iodine when iodide is oxidized by nitrite in an acid solution. The iodine is detected by extracting it with carbon tetrachloride.

Pipet 1 ml of the Fusion Solution into a 15 ml ground-glass stoppered centrifuge tube. Add 0.2 ml of CCl_4 and then add dropwise 1 ml of 3 F H_2SO_4. Add 1 ml of 1 F $NaNO_2$, stopper the tube, and shake for 20-30 seconds (Note 1). (Pink to red-violet color in the CCl_4: presence of iodine. Note 2.)

Notes.

1. A considerable pressure of CO_2 and of oxides of nitrogen may develop in the tube when it is shaken; for this reason the stopper should be removed carefully.
2. A perceptible pink color in the CCl_4 is given by 3 gamma of iodine.

P. II Precipitation of the Halogen Group

In this procedure the Fusion Solution is acidified and the Halogen Group Elements are precipitated as the silver halides. Alternative options are used, depending upon the absence or presence of iodine.

Pipet 10 ml of the Fusion Solution into a 15 ml glass stoppered graduated centrifuge tube and treat the solution by either Option A or Option B.

Option A (Iodine Absent--see Note 1). Prepare a blank for the detection of the Halogen Group by adding 10 ml of the blank fusion solution to another centrifuge tube. (Throughout this procedure treat the blank as the sample solution is treated; use the blank as a comparison. See Note 2.)

Add 9 F $HClO_4$ to the solution, dropwise and with stirring, until a pH of 3-4 is obtained as shown by wide-range indicator paper; then stir the solution vigorously (Notes 4 and 5). (If a glass capsule was used to contain the sample

during fusion, see Note 3.) Add by means of a pipet 0.2 ml of 9 F $HClO_4$ (Note 6). Finally add 1 drop of 1 F $AgNO_3$. (Precipitate: presence of bromine and/or chlorine. Note 7.)

If a Halogen Group precipitate is absent, transfer the solution to a 30 ml graduated centrifuge tube. Wash the 15 ml tube with one 1 ml portion of water; add the washing to the solution. Treat the solution by P. III.

If a Halogen Group precipitate is present, add 1 F $AgNO_3$, dropwise, and with stirring until no more precipitate forms (Note 8); centrifuge if necessary to detect the effect of successive additions. Stopper the centrifuge tube and shake it vigorously for 1 minute. Remove the glass stopper (Note 9), and centrifuge until the solution is perfectly clear (Note 10). Treat the mixture by the last paragraph of this procedure.

Option B (Iodine Present--see Notes 1 and 10). Add 0.2 ml of 1 F $AgNO_3$. Stopper the tube and shake it vigorously for 1 minute (Notes 4 and 11). Add 9 F $HClO_4$ to the solution, dropwise and with stirring, until a pH of 3-4 is obtained as shown by wide-range indicator paper (Note 4). Add by means of a pipet 0.2 ml of 9 F $HClO_4$. Stir the mixture (Note 7). Centrifuge until the solution is clear (Note 9). Add 1 drop of 1 F $AgNO_3$ to the centrifugate to be sure that the Halogen Group is completely precipitated.

With the aid of a dropper transfer the centrifugate (see Operation 1, Appendix V) to a 30 ml graduated centrifuge tube. Wash the precipitate (see Operation 2, Appendix V) with 1 ml of 0.01 F $HClO_4$ (Note 12). Add the washings to the centrifugate. Treat the precipitate by P. II-1 (Note 13). Treat the solution by P. III.

Notes.

1. If iodine is absent, the solution is acidified prior to the addition of $AgNO_3$. In this case, a Halogen Group precipitate constitutes a detection of bromine and/or chlorine. If no Halogen Group precipitate is obtained, bromine and chlorine can be assumed to be absent.

If iodine is present, iodide is precipitated (as AgI) before the solution is acidified (see Note 11).

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2. Halogen Group Elements present as impurities from the reagents, especially chloride from the Na_2O_2 and H_2O_2 used in P. I, are detected in this blank. If the amount of silver halide precipitate from the Fusion Solution is no greater than that from the blank fusion solution, the Halogen Group can be considered absent. The blank may be discarded when this procedure is completed.

A provision for the estimation of the chloride impurities from the reagents is made in Note 11 of P. II-6.

3. If a glass capsule has been used to contain the sample in P. I, treat the solution as follows:

> Add 6 F NaOH to a pH of 7-8 (not less than 7). (White precipitate: presence of silica.)
>
> Heat the mixture in a bath of boiling water for 3 minutes. Shake the mixture 1 minute. Cool to room temperature, and centrifuge. Transfer the centrifugate to a 30 ml centrifuge tube.
>
> Wash the precipitate as follows: Add 1 ml of water to it, break it up with a stirring rod, and boil the mixture in the centrifuge tube for 30 seconds (see Operation 4, Appendix V). Centrifuge and add the centrifugate to the 30 ml tube. Repeat this washing with another 1 ml portion of water. Reserve the precipitate for later treatment (see Note 6). Treat the centrifugate in the 30 ml tube by the procedure above, beginning with the addition of 9 F $HClO_4$ to a pH of 3-4.

This procedure removes all but 0.3-0.5 mg of silicon from the 10 ml portion being analyzed.

Since the 30 ml tube has no glass stopper, the solution cannot be shaken to coagulate any Halogen Group precipitate, as is recommended usually (see Note 9). In this case, coagulation may be obtained by immersing the tube in a bath of boiling water for 3-5 minutes and stirring the mixture occasionally.

4. About 2 ml of the 6 F $HClO_4$ will be required. Carbon dioxide is evolved when the solution is acidified. If this acidification is not made carefully, or if the solution is not stirred vigorously after acidification, the solution will foam and overflow. The instances of neutralization is usually indicated by the fact that bubbles of CO_2 are no longer immediately evolved on addition of the acid.

See Operation 5, Appendix V regarding the use of wide-range indicator paper.

Since the volume of the solution in this procedure is so large as to nearly fill the tube, the wash water generally used to rinse stirring rods and glass stoppers must not be used until the mixture has been centrifuged and the centrifugate transferred to the 30 ml tube.

5. Information as to the presence of certain metallic ions may be gained during the acidification: (1) a precipitate forming as the pH of the solution approaches 7 and which dissolves on further acidification indicates, if it is white, the presence of lead, zinc, aluminum, tin, antimony, or cadmium, or if it is blue or green, the presence of copper or chromium; (2) a white precipitate which remains after acidification of the solution indicates the presence of tin, antimony, or silicon; (3) a yellow precipitate which remains after acidification indicates the presence of lead or tin together with chromium as chromate.

6. A white or yellow precipitate may remain after the final addition of acid. Such a precipitate will indicate the presence of silica or hydrous stannic oxide or hydrous antimony oxide together with any tellurate, arsenate, phosphate, or chromate adsorbed on it, or lead chromate. It is desirable to remove these substances before the precipitation of the silver halides, since otherwise the subsequent amalgamation would be difficult. Any precipitate here is reserved and will be treated by the provisions made for it in the Arsenic Group procedures, in order to recover any Arsenic Group elements that may be present in it.

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In case a precipitate has been produced upon acidification and $AgNO_3$ has not been added previously, proceed as follows:

> Centrifuge the solution containing the precipitate and transfer the centrifugate to a 15 ml ground-glass stoppered graduated centrifuge tube. Do not wash the precipitate. Treat the centrifugate by the third paragraph above, beginning with the addition of 1 drop of 1 F $AgNO_3$. Reserve the precipitate for later treatment, as follows:
>
> If the precipitate is yellow, or if chromium is detected in P. III-1, this precipitate will be treated by Note 5, P. III-2.
>
> If chromium is found absent, and if tellurium is present, as shown by P. III-a, this precipitate will be treated by Note 2, P. III-d.
>
> If chromium and tellurium are found absent, and if arsenic is present, as shown by P. III-c, this precipitate will be treated by Note 1, P. III-4.
>
> If chromium and tellurium and arsenic are found absent, and if phosphorus is present, as shown by P. III-d, this precipitate will be treated by Note 1, P. III-7.
>
> If chromium, tellurium, arsenic, and phosphorus are found absent, discard the precipitate.

7. The colors of the halide precipitates are: AgI, pale yellow; AgBr, white or pale yellow; AgCl, white. The silver halides darken rapidly to a gray or blue color on standing. The color of AgBr is not detectible when the precipitate is small or when a large amount of AgCl is present.

If Option B of this procedure has been performed, the precipitate will be brown, due to a small amount of Ag_2O which does not dissolve in the acid solution.

If silicon is present in the sample or if a glass capsule has been used to contain the sample in P. I, a precipitate of silicic acid may separate with any silver halide precipitate that may form. This precipitate will be dissolved by the NaOH used in P. II-1.

8. The minimum amount of $AgNO_3$ should be used; otherwise, selenate, if present in large amounts, will be partially precipitated as silver selenate. One drop (0.03 ml) of 1 F $AgNO_3$ is equivalent to 1.0 mg of chlorine, 2.5 mg of bromine, or 3.8 mg of iodine. Therefore, not more than 0.25 ml of 1 F $AgNO_3$ should ever be required.

9. A small amount of silver halide precipitate tends to remain dispersed, but is usually effectively coagulated by shaking. If, after centrifugation, the solution is still turbid, the tube should be immersed in a bath of boiling water and stirred occasionally for a period of 3-5 minutes and then centrifuged again.

10. If iodine is present, $AgNO_3$ is added prior to acidification of the solution. This is necessary because nitrogen, if present in the sample, will be present, partially at least, as nitrite in the Fusion Solution. Nitrite oxidizes iodide to iodine in an acid solution; therefore, AgI is precipitated before the solution is acidified.

11. A brown precipitate of Ag_2O forms when $AgNO_3$ is added. Silver iodide is less soluble than Ag_2O so that part of the latter precipitate is metathesized to AgI during shaking.

The mixture should not be allowed to stand longer than necessary before the subsequent acidification since an aged Ag_2O precipitate does not readily dissolve when the solution is subsequently acidified.

12. When the silver halide predipitate is being broken up during washing it should not be pressed against the bottom of the centrifuge tube. It adheres tenaciously to the glass surface and, when treated with NH_4OH and amalgamated zinc in P. II-1, dissolves only slowly.

13. A fresh silver halide precipitate is decomposed in P. II more readily than an aged one; therefore the precipitate should not be allowed to stand more than an hour or half-hour.

P. II-b

Qualitative Test for Bromine

This test is to be performed only (a) if iodine is present in the Fusion Solution or (b) if a Halogen Group precipitate was obtained in Option A of P. II.

This sensitive qualitative test is made so that, in the absence of bromine, P. II-4 and P. II-5 can be eliminated. The test depends upon the oxidation of bromine by chloramine T ($CH_3C_6H_4SO_2NClNa$) and the consequent bromination of phenol red, resulting in the formation of an intense purple color.

If iodine and chromium are absent (Note 1), pipet 1 ml of the Fusion Solution into a 15 ml centrifuge tube. Prepare a blank by pipetting 1 ml of the blank fusion solution into another centrifuge tube. (Throughout this procedure, treat the blank as the sample solution is treated; use the blank as a comparison solution.)

Add 9 F $HClO_4$ to a pH of 3 as shown by wide range indicator paper. Add 3 ml of water in such a way as to wash down the sides of the tube. Using NaOH and $HClO_4$, adjust the pH of the solution to 5-7. Add 0.5 ml of a buffer solution which is 0.5 F in Na_2HPO_4 and 0.5 F in NaH_2PO_4 (Note 2). Centrifuge the solution (Note 3). If a precipitate is present, pour the centrifugate into another centrifuge tube and discard the precipitate. Add 3 drops of 0.01% phenol red solution to the clear solution. Add 2-3 mg (but no more) of solid chloramine T to the solution and stir for 60-75 seconds; then add 4-5 drops of 0.5 F $N_2H_4.HClO_4$ and stir well. (Violet or purple color: presence of bromine. Note 4.)

Notes.

1. The presence or absence of iodine is indicated by P. II-a. The absence of chromium is indicated by a colorless Fusion Solution (since 4 gamma per ml of chromium as chromate in the Fusion Solution impart to it a light yellow color).

Iodine, if not removed, would interfere with this test by giving a color similar to that given by bromine; chromium would interfere by preventing the violet or purple test color from appearing. Therefore, provision is made for oxidizing iodide to iodine and expelling the iodine by boiling, and for reducing chromate to chromic ion.

If iodine is present, or if the solution is colored, proceed as follows:

Pipet 1 ml of the Fusion Solution into a 50 ml conical flask. Prepare a blank by pipetting into a 50 ml flask 1 ml of the blank fusion solution. (The blank, which is used as a comparison for the sample solution, is treated throughout this procedure as is the sample solution.) Add 10 ml of water

and 1 ml of 3 F H_2SO_4. Heat the solution to boiling and then add 15-20 drops of 1 F $NaNO_2$. Boil the solution for 45-60 seconds while constantly swirling it. Add 2 ml of water and 10 drops of 1 F $NaNO_2$; again boil the solution for 45-60 seconds but do not evaporate to less than 8 ml. Cool the solution and transfer it to a 15 ml centrifuge tube. Add 6 F NaOH until the pH of the solution is greater than 5. Adjust the pH to 5-7 with $HClO_4$ and NaOH; then treat the solution by the procedure above, beginning with the addition of the Na_2HPO_4-NaH_2PO_4 buffer solution. Use 6-7 mg of chloramine T instead of 2-3.

2. It is essential that the solution be buffered. At a pH greater than 7 the chloramine T does not oxidize small amounts of bromide; at a pH less than 4 the bromination product of phenol red is yellow.

3. The following elements, if present, will precipitate completely or partially from the solution as phosphates, hydrated oxides, or hydroxides: dipositive copper, dipositive lead, dipositive zinc,(dipositive cobalt,)quadrapositive tin, and(aluminum). Some of these precipitates are difficult to see unless centrifuged to the bottom of the tube

4. A perceptible violet color is given by 2 gamma of bromine.

After the addition of the 0.5 F $N_2H_4.HClO_4$, the blank should be yellow or very slightly pink. A definite purple color in the blank indicates that the reagents used in P. I or in this procedure contain significant amounts of bromine or iodine and that fresh or pure reagents should be used.

Occasionally the sample solution is finally only a pale pink color. In order to decide as to the presence of significant amounts of bromine in such cases, an amount of KBr test solution containing 4-6 gamma of bromine should be added to 1 ml of the blank fusion solution and this solution treated as was the sample solution, and the resulting color compared with it.

As an additional aid in determining whether a significant amount of bromine is present in the sample, it should be noted that the purple color arising from the presence of 8 gamma of bromine appears much more rapidly than that given by only 4 gamma.

(A large amount of vanadate interferes in this test by preventing the violet or purple test color from appearing)

P. II-1

Removal of Silver

A solution of the halides is obtained in this procedure by treating the silver halide precipitate with amalgamated zinc. The silver is reduced to elementary silver.

Add 3 drops of 15 F NH_4OH and 3 drops of 6 F NaOH to the Halogen Group precipitate from P. II; stir the mixture, loosening any precipitate which may adhere to the centrifuge tube(Note 1). Add 0.3 ml of amalgamated zinc (Note 2). By means of the paddle-shaped end of a stirring rod, stir the mixture vigorously for 2 minutes by twirling the stirring rod between the fingers. Add 6 F NH_4OH (Note 3), [illegible], washing the stirring rod, until the volume of the solution is 3 ml. Add 1 small drop of mercury, stopper the centrifuge tube, and shake the mixture for

one minute (Notes 4 and 5). Transfer the solution by means of a dropper to a 50 ml conical flask and wash the amalgam with two 1 ml portions of water, adding the washings to the solution. Discard the amalgam. Gently boil the solution over an open flame for just 1 minute, while swirling continually (Note 6). Cool the solution. Add 9 F $HClO_4$ to a pH of 2-3 as shown by wide range indicator paper, and add 2 drops of the acid in excess (Note 7).

If both iodine and bromine are absent, as shown by P. II-a and P. II-b, treat the solution by P. II-6.

If either iodine or bromine are present, transfer the solution with a dropper to a 15 ml glass stoppered centrifuge tube; use two 1 ml portions of water to wash the flask. Add the washings to the solution.

If iodine is present, add 0.1 ml of 9 F $HClO_4$ and treat the solution by P. II-2. If iodine is absent but bromine is present, add 0.5 ml of 9 F $HClO_4$ and treat the solution by P. II-4.

Notes.

1. Zinc amalgam reduces silver halide slowly but reduces the $Ag(NH_3)_2^+$ ion rapidly.

2. Prepare the amalgamated zinc just before use as follows:

> Measure out into a 15 ml glass stoppered centrifuge tube about 0.3 ml of granulated zinc, 20 mesh. Add 1 ml of $Hg(C_2H_3O_2)_2$ reagent (0.03 F in $Hg(C_2H_3O_2)_2$ and 0.03 F in $HClO_4$). Stopper the centrifuge tube and shake it for about one-half minute. Thoroughly wash the granules of amalgamated zinc with water.

3. If a glass capsule was used to contain the sample during fusion, the mixture must now be transferred from the 30 ml centrifuge tube (see Note 3, P. II) to a glass stoppered, 15 ml centrifuge tube.

4. Whenever a glass stopper is removed from a centrifuge tube, it should be rinsed with a few drops of wash solution, generally water.

5. The solution may be slightly turbid at this point due to solid impurities introduced by the amalgamated zinc; disregard this turbidity.

6. The solution is heated in order to remove most of the NH_4OH; otherwise, so much 9 F $HClO_4$ is required for neutralizing the solution that NH_4ClO_4 may precipitate.

7. A white precipitate of $Zn(OH)_2$ may form when a pH of about 7 is reached, but it dissolves when the solution is acidified.

P. II-2 Detection and Separation of Iodine

In this procedure iodide is oxidized to iodine by nitrite and then extracted from the aqueous solution with CCl_4.

To the solution from P. II-1 add 4 ml of CCl_4 (Note 1) and 0.2 ml of 1 F $NaNO_2$. Shake the mixture for 1 minute. Allow the layers to separate; centrifuge for 20-30 seconds if necessary. (Red-violet color in the CCl_4 phase: presence of iodine. Note 2.)

Shake the mixture gently so that any CCl_4 floating on the surface of the aqueous phase sinks. Remove the CCl_4 from the centrifuge tube with a dropper and transfer it to a ground glass stoppered centrifuge tube. Repeat the extraction with 1 ml portions of CCl_4 until the CCl_4 phase remains colorless (usually three extractions are sufficient). If the third extract is not colorless, add an additional 0.03 ml portion of 1 F $NaNO_2$. To the combined CCl_4 extracts add 1 ml of water, stopper the tube, and shake gently for 5-10 seconds. Allow the layers to separate. Remove the wash water and add it to the aqueous solution. Treat the combined CCl_4 solutions by P. II-3; treat the aqueous solution by P. II-4 if bromine is present or by P. II-6 if bromine is absent.

Notes.

1. Unpurified reagent grade CCl_4 contains impurities capable of reacting with iodine and bromine. The CCl_4 used in this procedure and in P. II-a and in P. II-4 should be purified according to the directions given in Appendix I.
2. Forty gamma of iodine will produce an easily perceptible color in the centrifuge tube; by transferring the CCl_4 solution to a small test tube (75 x 10 mm or smaller) and looking lengthwise through the tube against a white background (at the same time using a similar tube containing CCl_4 as a blank) 15 gamma of iodine can be detected readily.

P. II-3 Estimation of Iodine

Iodine is estimated in this procedure by adding an aqueous iodide solution to the carbon tetrachloride solution of iodine and titrating the mixture with thiosulfate.

Wash the CCl_4 solution from P. II-2 at least 4 times by shaking it gently with 0.5 ml portions of sodium monohydrogen phosphate-sodium dihydrogen phosphate

buffer solution (Notes 1, 2, and 3). Discard the washings.

Flush the air from a 50 ml ground-glass stoppered flask with CO_2 (Note 4). Transfer the CCl_4 solution with a dropper to the flask. Wash the centrifuge tube with 5 ml of water. Add 0.2 ml of 6 F $HC_2H_3O_2$ and 5 ml of 0.1 F KI (Note 5). Titrate with standard 0.02 F $Na_2S_2O_3$, shaking occasionally until the iodine color is faint. Add 0.2 ml of starch indicator solution and titrate until the solution is colorless. From the volume of $Na_2S_2O_3$ used, calculate the percent of iodine in the sample (Note 6).

Notes.

1. See Appendix I for the preparation of the buffer solution which is 0.5 F in sodium monohydrogen phosphate, and 0.5 F in sodium dihydrogem phosphate.
2. If nitrous acid and the oxides of nitrogen are not removed by these washings, they will interfere with the estimation by oxidizing some of the iodide subsequently added. These acidic oxidizing agents are more rapidly removed by washing with a buffer solution which has a pH of approximately 7 than by washing with water. The last washing should be tested for the presence of nitrite by adding the washing to a solution of 1.5 F H_2SO_4 faintly colored with 0.01 F $KMnO_4$; if nitrite is present, it reduces the permanganate, decolorizing the solution.
3. The CCl_4 extracts should not be washed with larger amounts of solution than is necessary or significant amounts of I_2 may be lost since the distribution ratio at 25° for the equilibrium of I_2 between CCl_4 and water is only 87.
4. The air is removed in order to minimize the oxidation of iodide.
5. An orange color appears in the aqueous phase when the iodide is added. The formation of the stable tri-iodide ion, I_3^-, causes I_2 to be withdrawn from the CCl_4 phase into the aqueous phase.
6. One ml of 0.02 F $Na_2S_2O_3$ corresponds to 2.54 mg of iodine.

P. II-4

Separation of Bromine

In this procedure bromide is oxidized to bromine by permanganate in a solution about 2.5 F in $HClO_4$. The bromine is extracted with CCl_4.

If bromine is present, as shown by P. II-b, either (a) treat the solution from P. II-1 by the third and subsequent paragraphs of this procedure beginning with the addition of 1.5 ml of 9 F $HClO_4$, or (b) treat the solution from P. II-2 by the next and subsequent paragraphs (Note 1).

If iodine was present, add 0.4 ml of 9 F $HClO_4$ to the aqueous solution from P. II-2. Transfer the solution from the centrifuge tube to a 50 ml conical flask. Wash the centrifuge tube with two 1 ml portions of water; add the washings

to the solution in the flask. Boil the solution (Note 2) until brown fumes are no longer evolved or until the odor of the oxides of nitrogen is no longer noticeable in the vapors, and then evaporate to 5-6 ml, but not less than 5 ml (Notes 3 and 4). Cool the solution (Note 5). If the solution is clear (Note 5), transfer it to a 15 ml ground glass stoppered centrifuge tube. Wash the flask with 1 ml of water, and add the washing to the solution in the centrifuge tube.

Add 1.5 ml of 9 F $HClO_4$ and 4 ml of purified CCl_4 to the solution (see Note 1, P. II-2). Shake the mixture (Note 6). Add 0.1 F $KMnO_4$ dropwise until a distinct and permanent purple color, equal in intensity to that given by 1 drop of the 0.1 F $KMnO_4$ in 3-4 ml of water, is obtained in the aqueous phase. Shake the mixture for 2 minutes; add more $KMnO_4$ if the color disappears. Shake the tube gently so that any CCl_4 floating on the surface of the aqueous phase sinks. With the aid of a dropper, remove the CCl_4 and add it to a ground glass stoppered centrifuge tube containing 0.5-1.0 ml of water (Note 7). (Yellow or brown color in the CCl_4 phase: presence of bromine. Note 8.) Repeat the extraction with three 1 ml portions of CCl_4. Treat the CCl_4 solution by P. II-5. Treat the aqueous solution by P. II-6 (Note 9).

Notes.

1. If P. II-2 has been performed, the nitrite used there must be removed prior to the addition of $KMnO_4$ in this procedure, since the nitrite would otherwise reduce an undesirably large amount of permanganate. The second paragraph of this procedure provides for the removal of nitrite by adding acid to the solution and boiling it.
2. The solution must be kept swirling or "bumping" and consequent loss of solution will occur.
3. The solution should not be evaporated to less than 5 ml or oxidation of any bromide or chloride may occur.
4. Occasionally, if only a small excess of nitrite is present, the brown fumes of NO_2 are not noticed, but the odor of the oxides is an adequate test. Familiarity with the odor may be obtained by boiling a solution of 1.5 F H_2SO_4 with a few drops of $NaNO_2$.
5. A white turbidity indicates the presence of silica. If the mixture is turbid, proceed as follows:

> Transfer the solution from the flask to a 15 ml centrifuge tube. Wash the flask with 1 ml of water and add the washing to the solution in the centrifuge tube. Centrifuge until the solution is clear. Transfer the centrifugate to a 15 ml ground glass stoppered centrifuge tube. Wash the precipitate with 1 ml of water; add the washing to the centrifugate. Discard the precipitate.

6. No iodine color should be observed in the CCl_4 phase. If such a color is observed, the separation of iodine has not been complete, and the CCl_4 phase here should be separated (and added to the CCl_4 extracts of P. II-3) and another 4 ml portion of CCl_4 added to the aqueous solution.

7. Since bromine is lost from carbon tetrachloride solutions by volatilization the CCl_4 is best transferred by immersing the tip of the dropper below the surface of the water in the centrifuge tube.

8. A perceptible color will be produced in the CCl_4 in the centrifuge tube by 0.25 mg of bromine. Even though the CCl_4 is colorless, the mixture should be treated by the remaining parts of this procedure and then by P. II-5. The appearance of a purple color when the starch solution is added in P. II-5 will indicate the presence of as little as 10 gamma of bromine.

9. The solution should not be allowed to stand more than 1 hour before treatment by P. II-6 or significant oxidation of any chloride present may occur and low results for chloride may be obtained.

P. II-5 Estimation of Bromine

Wash the CCl_4 solution with two or three 0.5 ml portions of water (Note 1). Discard the washings. Flush the air from a 25 ml ground glass stoppered flask with CO_2. Transfer the CCl_4 solution to the flask, using 5 ml of water (see Note 7, P. II-4). Add 5 ml of 0.1 F KI and shake vigorously. Add 0.1 ml of 6 F $HC_2H_3O_2$ and titrate with standard 0.02 F $Na_2S_2O_3$, shaking vigorously, until the color begins to fade. Add 0.2 ml of starch indicator and titrate to a colorless solution. From the volume of the $Na_2S_2O_3$ used, calculate the percent of bromine in the sample (Note 2).

Notes.

1. The last portion of wash water should not be colored with permanganate and should be free from any brown precipitate of MnO_2. If it is not, the CCl_4 should be washed until it is. Care should be taken to use the minimum amount of wash water. The distribution ratio at 25° C for the equilibrium of Br_2 between CCl_4 and water is 27.

2. One ml of 0.02 F $Na_2S_2O_3$ corresponds to 1.60 mg of bromine.

P. II-6 Detection and Estimation of Chlorine

Optional methods, mercurimetric and argentimetric, are provided for detecting and estimating chlorine. In the mercurimetric method, diphenyl carbazone is used as an indicator, and the chloride is titrated with a standard mercuric nitrate solution. Unionized mercuric chloride is first formed; the end-point is given by the formation of the violet colored mercuric diphenylcarbazone compound. The argentimetric method is the classical Mohr titration with silver nitrate using chromate as the indicator. The mercurimetric method is less critically

dependent upon the adjustment of the pH of the solution, the presence of other ions, and the experience of the analyst; its use is recommended.

Mercurimetric Method:

If iodine and bromine were absent, treat the solution from P. II-1, contained in a 50 ml conical flask, by the fourth and last paragraphs of this procedure, beginning with the addition of 2,4-dinitrophenol.

In case iodine was present and bromine was absent, (i.e., if P. II-2 has been performed but P. II-4 has not) (Note 1), transfer the solution from P. II-2 to a 50 ml flask. Wash the centrifuge tube with two 1 ml portions of water and add the washings to the solution in the flask. Add 0.4 ml of 9 F $HClO_4$, and, while swirling the flask, heat the solution to boiling temperature and then boil for 2-3 minutes. Cool the solution. Treat the solution by the fourth and last paragraphs of this procedure, beginning with the addition of 2,4-dinitrophenol.

In case bromine was present (i.e., if P. II-4 has been performed) (Note 2), transfer the solution from P. II-4 to a 50 ml flask. Wash the centrifuge tube with two 1 ml portions of water and add the washings to the solution in the flask. Add 3% H_2O_2, dropwise and with swirling, until the solution is colorless. Then add 1 drop in excess. Add 2.8 ml of 6 F NaOH and 4 drops of 0.2% 2,4-dinitrophenol. While swirling, add 1 F NaOH dropwise until the yellow end-point is nearly reached (Note 3). Then add 0.1 F NaOH dropwise until a permanent yellow color is obtained; the pH should be 4-5 on wide range indicator paper. Treat the solution as directed in the last paragraph.

Add 4 drops of 0.2% 2,4-dinitrophenol, then add 3 F NaOH dropwise until the solution becomes yellow. With 0.1 F $HClO_4$ reduce the color to a light yellow; the pH should be 4-5 on wide range indicator paper (Note 4).

Pipet into the solution exactly 1 ml of 0.25 F HNO_3 and 0.5 ml of 0.1% diphenylcarbazone indicator (Note 5), and dilute to 20 ml with water (Note 6). Prepare a blank (Note 7), and add to it standard 0.015 F $Hg(NO_3)_2$ from a syringe buret until a pale violet color is obtained (Note 8). To the solution being analyzed add 0.04-0.05 ml of the standard $Hg(NO_3)_2$ solution. (Violet color: absence of

chlorine. Note 9.) If the solution remains colorless, continue the titration with $Hg(NO_3)_2$ until its color matches that of the blank (Note 10). From the volume of $Hg(NO_3)_2$ used, calculate the percent of chlorine in the sample (Note 11).

Notes.

1. Nitrite was added to the solution in P. II-2. If P. II-4, the "Detection and Separation of Bromine", was not performed, the nitrite must be removed in this procedure (P. II-6), since it would otherwise destroy the diphenylcarbazone indicator subsequently added. The second paragraph of this procedure provides for the removal of nitrite by adding acid to the solution and boiling it.

2. Permanganate was added to the solution in P. II-4. The permanganate and any MnO_2 must be removed in this procedure since they would otherwise interfere with the colors obtained subsequently. The third paragraph of this procedure provides for their removal by the addition of H_2O_2.

3. Local precipitates of brown MnO_2 will form around the drops of the NaOH. The brown precipitate dissolves easily with swirling but will begin to persist as the solution approaches neutral. The increasing persistence of the brown MnO_2 color and the yellow dinitrophenol color indicate the point to change to 0.1 F NaOH. If the solution becomes basic a permanent precipitate will be obtained. In this case add 6 F NHO_3 until the solution has a pH of less than 4. Decolorize the solution with 3% H_2O_2 and neutralize to the yellow color with 0.1 F NaOH.

4. A white turbidity indicates the presence of silica. If the mixture is turbid, remove the silica as follows:

> Transfer the solution from the flask to a 15 ml centrifuge tube. Wash the flask with 1 ml of water and add the washing to the solution in the centrifuge tube. Centrifuge the mixture. Transfer the centrifugate to a 50 ml flask. Wash the precipitate with 1 ml of water; add the washing to the centrifugate. Discard the precipitate.

5. The solution of diphenyl carbazone is somewhat unstable. It should be protected from light and, if more than 2-3 weeks old, should be either discarded or tested before use by preparing the blank.

6. The final volume of solution should be accurate to within 2 or 3 ml. The volume can be conveniently estimated by using as a comparison another 50 ml flask which contains just 20 ml of water.

7. The blank is prepared as follows:

> If the procedure for the separation of bromine (P. II-4) has not been performed, add 10 ml of water and 0.2 ml of 9 F $HClO_4$ to a 50 ml conical flask; if P. II-4 has been performed, add 10 ml of water and 1.5 ml of 9 F $HClO_4$ to a 50 ml flask. Proceed as directed in the fourth paragraph of this procedure.(P. II-6).

8. Less than 0.04 ml of standard 0.015 F $Hg(NO_3)_2$ solution should be required by the blank. If a larger amount of $Hg(NO_3)_2$ is required it is probable that either (a) a relatively large amount of chloride impurity is present in the reagent solutions or (b) the diphenyl carbazone solution has partially decomposed.

9. Forty gamma of chloride can be detected. However, since the reagents used, particularly those used in P. I-A and P. I-B contain chloride as an impurity (see Note 11), a detection of small amounts of chloride here does not necessarily indicate the presence of chlorine in the sample.

10. Swirl the solution well and allow it to stand for a few seconds to reach equilibrium before matching the colors.

11. An end-point correction must be made by subtracting the volume of $Hg(NO_3)_2$

used by the blank from the volume of $Hg(NO_3)_2$ used by the sample. One ml of 0.015 F $Hg(NO_3)_2$ corresponds to 1.06 mg of chlorine.

The Fusion Solution may contain chloride from the reagents, especially the reagents used in P. I. Therefore, if a significant amount of precipitate was obtained in the blank precipitation of the Halogen Group, and if the amount of chlorine found in the sample is small, an estimation of the chloride present in the reagents should be made. This is easily done by adding 5 ml of the blank fusion solution to a 50 ml flask, adding 9 F $HClO_4$ until the pH of the solution is 2-4, and then treating it by the fourth and subsequent paragraphs of this procedure. Remember that only 5 ml of blank fusion solution were used, whereas the analysis of the sample used 10 ml of Fusion Solution.

Optional Argentimetric Method:

In case neither iodine or bromine has been extracted, transfer the solution from P. II-1 to a 50 ml conical flask; use two 1 ml portions of water to rinse the centrifuge tube. Treat the solution by the fourth and fifth paragraphs of this procedure, beginning with the addition of HNO_3.

In case iodine has been extracted (P. II-2) and bromine has not been extracted (P. II-4), transfer the solution from P. II-2 to a 50 ml conical flask; use two 1 ml portions of water to rinse the centrifuge tube. While swirling the flask, boil the solution for 30-45 seconds or until the odor of the oxides of nitrogen is no longer perceptible. Treat the solution by the fourth and fifth paragraphs of this procedure.

In case bromine has been extracted (P. II-4) transfer the solution to a 50 ml flask; use 1 ml of water as wash solution. Add 1.5 F Na_2CO_3 until a pH of 8 as indicated by wide range indicator paper, is obtained; then add 1 ml of Na_2CO_3 in excess. Heat the solution to boiling, and, if a permanganate color is not present, add 0.1 F $KMnO_4$ dropwise until such a color is obtained (Note 1). Add 0.1 ml of 30% H_2O_2. Evaporate the solution to 7-8 ml. Cool, and transfer it to a 15 ml centrifuge tube using two 1 ml portions of water to rinse the flask. Centrifuge (Note 2) and transfer the solution to a 50 ml conical flask. Wash the residue in the centrifuge tube with 1 ml of water and combine the washing with the solution in the 50 ml flask.

Add dropwise to the solution in the flask 6 F HNO_3 until a pH of 3 is obtained. Boil the solution for a few seconds, cool, and add 1 drop of phenolphthalein indicator. Add 3 F NaOH until a pink color appears, then just discharge the

pink color with 0.1 F $HClO_4$ (Note 3). Centrifuge the solution if a precipitate (of silica) is present. Add to the clear solution 1 drop of standard 0.025 F $AgNO_3$. (White precipitate: presence of chlorine.)

If a precipitate is produced, add 1 drop of 1 F K_2CrO_4 and titrate with standard 0.025 F $AgNO_3$ until the first brownish turbidity is observed (Note 4). From the volume of $AgNO_3$ used, calculate the percent of chlorine in the sample (Note 5).

Notes.

1. This further excess of $KMnO_4$ is added to oxidize the manganous ion formed during the bromine extraction. By the subsequent addition of H_2O_2, the excess permanganate is reduced in a basic solution, and thus all the manganese is removed as MnO_2. Any manganous salts left in the solution will interfere with the end-point of the titration as such salts are oxidized by the oxygen of the air and by the chromate indicator in even slightly alkaline solutions with the formation of a greenish precipitate of chromic hydroxide.

2. The precipitate contains besides the manganese, some basic zinc carbonate; zinc was introduced into the solution in P. II by the zinc-amalgam treatment of the ammonia . . . solution.

3. At this point the pH of the solution should be approximately 7, as shown by wide-range paper. The lowest pH permissible is fixed by the solubility of silver chromate in acid solutions; the highest pH by the insolubility of silver oxide.

4. Prepare a blank and make an end-point correction for the chloride titration as follows:

> Into a 50 ml flask measure 2 ml of 3 F NaOH and 2.5 ml of 9 F $HClO_4$. Add 1.5 F Na_2CO_3 to a pH of 8 and then 1 ml in excess. Add 6 F HNO_3 to a pH of less than 3 and boil for a few seconds. Cool, add 1 drop of phenolphthalein indicator and 3 F NaOH to a pink color. Just discharge the pink color with 0.1 F $HClO_4$ (the pH should be about 7).
>
> Add 1 drop of 1 F K_2CrO_4 and <u>just enough</u> finely powdered $CaCO_3$ to match the AgCl turbidity of the chloride sample. The $CaCO_3$ must be precipitated material, must be chloride free, and must be shaken vigorously to disperse it throughout the solution. Titrate with standard 0.025 F $AgNO_3$ until the brownish color matches that of the titrated mixture. Subtract the volume of $AgNO_3$ used for the blank from the volume used for the chloride sample.

5. One ml of 0.025 F $AgNO_3$ corresponds to 0.89 mg of chlorine.

Tabular Outline III

The Analysis for the Arsenic Group Elements

Precipitate from P. III: Ag_2CrO_4, $Ag_2H_4TeO_6$, Ag_3AsO_4, Ag_3PO_4, Ag_2CO_3.

P. III-1. Add $HClO_4$, water, and HCl.

Precipitate: AgCl.	Solution: $HCr_2O_7^-$, $H_4TeO_6^{=}$, H_3AsO_4, H^+Cl^-.
Discard.	P. III-2. Estimate amount of chromium colorimetrically.
	P. III-3. Add $N_2H_4.H_2O$. Heat.

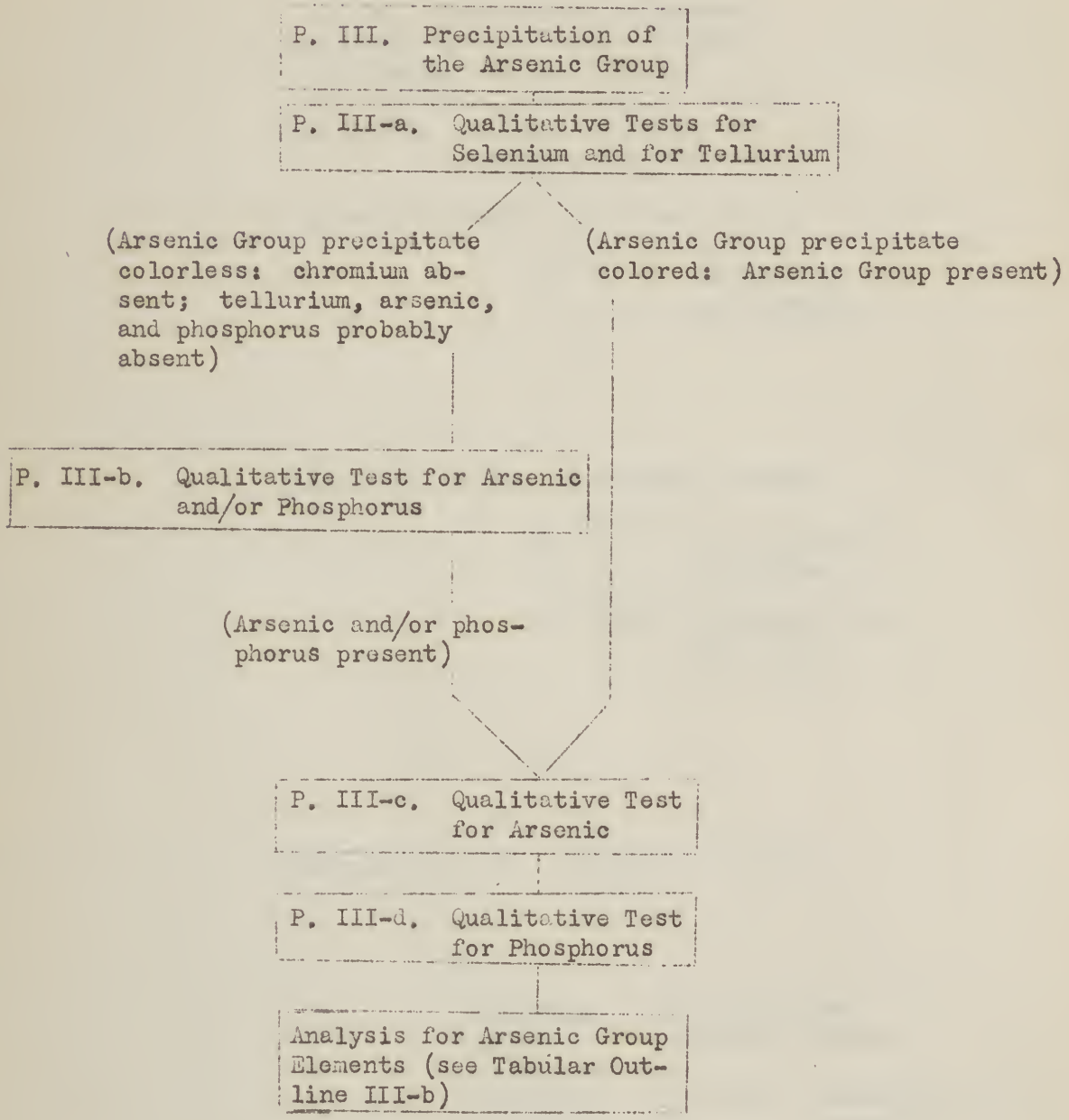
Precipitate: Te	Solution: H_3AsO_3, H_3PO_4, Cr^{+++}, $N_2H_5^+$, H^+Cl^-.
P. XIX-1. Add HCl and ICl.	[P. III-4 (performed only if Cr and Te are absent).
(H_2TeO_3, I_2, ICl_2^-, H^+Cl^-)	(H_3AsO_4, H_3PO_4, H^+Cl^-)
Add CCl_4. Titrate with $KH(IO_3)_2$.	Add KI.
(H_2TeO_3, ICl_2^-)	(H_3AsO_3, H_3PO_4, I_3^-)
	Titrate with $Na_2S_2O_3$.
	(H_3AsO_3, H_3PO_4, I^-, $S_4O_6^{=}$)]

P. III-5. Add KI and $Na_2S_2O_3$ if Cr and/or Te is present. Saturate with H_2S.

Precipitate: As_2S_3.	Solution: H_3PO_4, Cr^{+++}, I^-, $S_4O_6^{=}$, H^+Cl^-.
P. III-6. Add NaOH and Br_2 water. Heat.	P. III-7. Evaporate. Add HNO_3. Again evaporate.
($AsO_4^{=}$, Br^-, BrO^-, BrO_3^-, Na^+OH^-)	(H_3PO_4, Cr^{+++}, HSO_4^-, $H^+NO_3^-$)
Add HCl and HCOOH.	Add $(NH_4)_2MoO_4$ reagent. Heat.
(H_3AsO_4, Br^-, HCOOH, CO_2, H^+Cl^-)	Precipitate: $(NH_4)_3PO_4.12MoO_3$. / Solution:
Add KI and HCl.	P. III-8. Add phenolphthalein. / Discard.
(H_3AsO_3, I_3^-, HCOOH, H^+Cl^-)	Titrate with NaOH.
Titrate with $Na_2S_2O_3$.	($HPO_4^{=}$, $MoO_4^{=}$, NH_4^+)
(H_3AsO_3, I^-, $S_4O_6^{=}$, HCOOH, H^+Cl^-)	

Tabular Outline III-a

Procedure Sequence for the Qualitative Tests for the Arsenic Group Elements



Tabular Outline III-b

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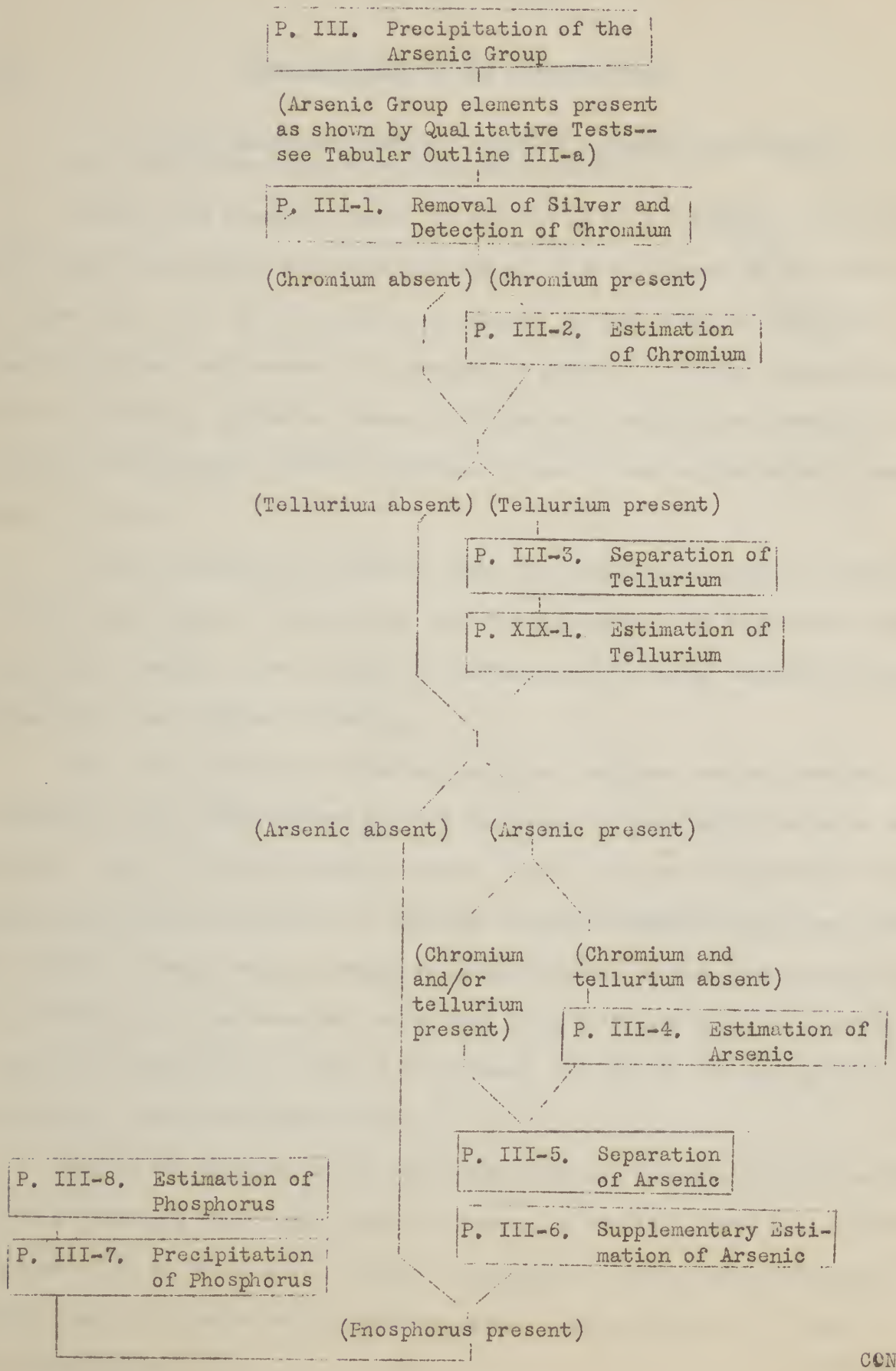
Procedure Sequence for the Analysis of the Arsenic Group



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THE ANALYSIS OF THE ARSENIC GROUP

(Cr, Te, As, P)

P. III

Precipitation of the Arsenic Group

In this procedure Ag_2CrO_4, $Ag_2H_4TeO_6$, Ag_3AsO_4, and Ag_3PO_4 are precipitated from a solution whose pH is 7.

To the cool solution from P. II add 0.2 ml of 1 F $AgNO_3$. Add 1.5 F Na_2CO_3 dropwise until the mixture is turbid and the pH is 5-6 as shown by wide range indicator paper (Note 1). If the mixture is colored but the color is indefinite, centrifuge the mixture and examine the precipitate (Note 2). (White precipitate: absence of chromium; probable absence of tellurium, arsenic, and phosphorus. Note 3. Colored precipitate: probable presence of one or more of the Arsenic Group elements. Note 4.)

If the precipitate is colored, make the qualitative tests as indicated in the "Instructions for the Selection of Qualitative Tests to Be Performed" (page 33) and in Tabular Outline III-a. Treat the mixture by the second paragraph below, beginning with the addition of Na_2CO_3.

If a white precipitate has been obtained, perform the qualitative tests as indicated in the "Instructions for the Selection of Qualitative Tests to Be Performed" (page 33) and in Tabular Outline III-a. If any of the Arsenic Group elements specifically tested for is present, treat the mixture by the paragraph below. If the Arsenic Group elements are absent, break up the white precipitate with a stirring rod, and transfer the mixture with a dropper to a 50 ml flask (Note 5). Wash the centrifuge tube with 1 ml of water and add the washing to the mixture in the flask. Treat the mixture by P. IV.

Add to the mixture in the centrifuge tube 1.5 F Na_2CO_3 dropwise until a pH of 7, as shown by wide range indicator paper, is obtained (Note 6). Stir the mixture well and centrifuge it. If the solution is not clear after thorough centrifugation, heat the mixture and centrifuge again. Add one drop of 1 F $AgNO_3$ to the clear centrifugate.

If a white precipitate is produced by this addition (Note 7), centrifuge the solution until clear; then transfer the centrifugate (see Operation 1, Appendix V) to a 50 ml flask. Wash the precipitate (see Operation 2, Appendix V) with 1 ml of water and add the washing to the centrifugate. Treat the precipitate by P. III-1, and treat the solution by P. IV.

If the addition of 1 drop of 1 F $AgNO_3$ produces a colored precipitate (Note 7), stir up the mixture well, add 1 drop of 1 F $HClO_4$, centrifuge, and add another drop of 1 F $AgNO_3$. Repeat this operation until the addition of a drop of $AgNO_3$ produces only white precipitate in the clear centrifugate. Centrifuge the mixture and transfer the centrifugate (see Operation 1, Appendix V) to a 50 ml flask. Wash the precipitate with (see Operation 2, Appendix V) 1 ml of water and add the washing to the centrifugate. Treat the precipitate by P. III-1. Treat the solution by P. IV.

Notes.

1. In the absence of the Arsenic Group elements a white turbidity of Ag_2CO_3 will be produced when the pH of the solution is increased to approximately 6.5; in the presence of large amounts of the elements in this group, precipitation of silver chromate, tellurate, arsenate, or phosphate will begin at lower pH values.

About 0.5-0.7 ml of Na_2CO_3 is usually required. Only the minimum amount of Na_2CO_3 required to produce a distinct turbidity should be added. The Na_2CO_3 should be added in such amount that only a distinct turbidity is produced; otherwise the Ag_2CO_3 will obscure the color of small amounts of silver tellurate, arsenate, phosphate, or chromate. If too much Ag_2CO_3 is precipitated, the solution should be cleared by the addition of a drop of 1 F $HClO_4$ and the Na_2CO_3 then added in smaller portions.

2. The wide range indicator paper must be used as carefully as possible if the determination of the pH is to be accurate to within one pH unit (see Operation 5, Appendix V).

The color of the paper should be noted after 15-20 seconds. On longer standing the color corresponding to a more alkaline pH will develop because of the loss of carbon dioxide from the solution on the paper.

3. This precipitate will always contain Ag_2CO_3. If much silicon is present, a suspended precipitate of silicic acid may form. Further, certain metallic elements such as lead, copper, cadmium, antimony, tin, zinc, and aluminum, which are soluble in the alkaline Fusion Solution, would appear in the Arsenic Group as, e.g., hydrous oxides, carbonates, chromates, tellurates, arsenates, or phosphates.

A white precipitate indicates the absence of chromium; even in the presence of metallic elements chromate will give a colored precipitate here. Small amounts of silver arsenate, tellurate, or phosphate may not be detected in the white precipitate. Also, certain metallic elements, such as lead, would dissolve in the strongly alkaline Fusion Solution and in the strongly acid solution present during the precipitation of the Halogen Group elements, but would be precipitated as arsenates, tellurates, or phosphates when the solution was neutralized with 1 F Na_2CO_3. Some of these salts are white rather than colored as are the corresponding

silver salts. For these reasons a white precipitate is not conclusive proof of the absence of tellurium, arsenic, or phosphorus.

4. The colors of the silver precipitates when present individually are: Ag_2CrO_4, red; $Ag_2H_4TeO_6$, brown; Ag_3AsO_4, red (pink in the presence of Ag_2CO_3); Ag_3PO_4, yellow.

The precipitate may be slightly discolored even when the Arsenic Group elements are absent.

A definite yellow color suggests that more than 80 gamma of phosphorus are present, and a tinge of pink or tan indicates the presence of more than 40 gamma of chromium, tellurium, or arsenic. In the presence of certain metallic elements, such as lead, the presence of chromium (as chromate) will be indicated by a yellow precipitate. If the color of the silver precipitate is indefinite, prepare a blank containing 0.03 ml of 1 F $AgNO_3$ in the same volume of solution and add 1 F Na_2CO_3 until the amount of turbidity equals that in the unknown. Centrifuge the two solutions and compare the colors of the precipitates. The Ag_2CO_3 precipitate in the blank should be pure white. If allowed to stand for any considerable length of time, the precipitate darkens.

5. In the absence of the Arsenic Group elements it is desirable that the white precipitate obtained in this procedure be combined with the centrifugate in order that any Sulfur Group elements which may have been precipitated (e.g., as $PbSO_4$ or Ag_2SeO_4) may be recovered.

6. The pH of the solution must be adjusted as closely as possible to 7. If the solution is made too alkaline, the silver is so completely precipitated as oxide or carbonate that significant amounts of the Arsenic Group elements may remain in the solution; also, any selenium may partially precipitate as Ag_2SeO_4. If the solution is too acid, significant amounts of the Arsenic Group elements may remain unprecipitated.

7. The $AgNO_3$ is added in order to insure that the pH is not too high. If the solution has been adjusted to the proper pH, all of the Arsenic Group elements will be in the precipitate; therefore, only a white precipitate of Ag_2CO_3 will be obtained when this addition of $AgNO_3$ is made. However, if the solution has been made too basic, and the silver has been so completely precipitated as oxide or carbonate that significant amounts of Arsenic Group elements are left in solution, the precipitate caused by this addition of $AgNO_3$ will be colored.

Instructions for the Selection of Qualitative Tests for Arsenic Group Elements to be Performed

Four qualitative tests for the Arsenic Group elements are provided. These tests have for their purpose the shortening and simplification of the analysis of the Arsenic Group. These tests are made on separate aliquots of the Fusion Solution. The order in which these tests should be performed is indicated in Tabular Outline III-a. Tabular Outline III-b indicates the sequence of the procedures of the Arsenic Group analysis and indicates which procedures may be omitted as a result of information obtained from the qualitative tests.

P. III-a provides for the detection of tellurium and of selenium. The tests of P. III-a should be performed in every case. If tellurium is absent, P. III-3 may be omitted.

P. III-b provides for the detection of arsenic and/or phosphorus; if it is negative, no further analysis for these two elements is necessary; if it is positive, P. III-c and P. III-d, the tests for arsenic and for phosphorus, must be performed. P. III-b should be performed only when the Arsenic Group precipitate obtained in P. III is white.

P. III-c provides for the detection of arsenic; if it is negative, P. III-4, P. III-5, and P. III-6 can be omitted. P. III-d provides for the detection of phosphorus; if it is negative, P. III-7 and P. III-8 can be omitted. P. III-c and P. III-d should be performed (a) when P. III-b has been performed and has given a positive result, or (b) when a colored Arsenic Group precipitate has been obtained in P. III.

No qualitative test for chromium is provided. When the other Arsenic Group elements are absent, the color of the Arsenic Group precipitate (see Note 3, P. III) provides an adequate detection of chromium. When other Arsenic Group elements are present, P. III-1 will provide the detection of chromium.

P. III-a Qualitative Tests for Selenium and for Tellurium

Selenium is detected and removed as the metal by treatment with hydroxylamine hydrochloride in the hydrobromic acid solution.

The test for tellurium utilizes, first, the yellow color formed when a hexapositive tellurium-hydrobromic acid solution containing hydrazine is heated, and secondly, the subsequent formation of a black turbidity or precipitate of tellurium metal.

Pipet 1 ml of the original Fusion Solution into a small test tube (75 x 10 mm). Prepare a blank by pipetting 1 ml of the blank fusion solution into another small test tube. Throughout this procedure, treat this blank as is the sample solution, and use it as a comparison solution.

Add to the solution 1 ml of 9 F HBr (Note 1) and 2 drops of 5 F $NH_2OH.HCl$, mix well, and heat in a bath of boiling water for 3-4 minutes. (Yellow or pink turbidity or red precipitate: presence of selenium. Yellow color in the solution: probable presence of tellurium. Colorless solution: absence of tellurium and selenium. Note 2.)

If selenium is present, heat the solution for an additional 2-3 minutes in a bath of boiling water (Note 3). Centrifuge (Note 4) and withdraw the centrifugate with a dropper; take care not to disturb the precipitate. Transfer the centrifugate to another test tube (Note 5). (Yellow solution: probable presence of tellurium.)

If selenium is absent, or has been removed, and the solution is colored, cool it to room temperature (Note 6), add by means of a pipet 0.1 ml of 85% $N_2H_4.H_2O$, mix well, and heat in a bath of boiling water for 2 minutes. (Black turbidity or precipitate: presence of tellurium. Note 7.)

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1. If the solution turns yellow immediately after the addition of HBr, the presence of ferric iron is indicated. This color will disappear after heating for several minutes with $NH_2OH.HCl$. The color from 60 gamma of iron will completely disappear after 3 minutes heating and thus will not interfere with the detection of tellurium or selenium.

A pink or rose color (colloidal metallic copper) indicates the presence of copper. If copper is present, add to the blank solution an amount of $Cu(NO_3)_2$ test solution sufficient to give an approximately matching rose color. With the aid of this blank solution, the yellow color imparted by 4 gamma of tellurium can be detected in the presence of 60 gamma of copper, and the yellow color imparted by 8 gamma of tellurium can be readily detected in the presence of 80 gamma of copper.

Chromate is reduced to tripositive chromium by the NH_2OH. The yellow color imparted by 4 gamma of tellurium can be detected in the presence of 100 gamma of chromium.

2. If as much as 3 gamma of selenium are present in the solution being tested a distinct pinkish color or turbidity will be visible.

The yellow color imparted by 3-4 gamma of tellurium, probably due to the formation of complex anions such as $TeBr_6^{=}$, is faint but is visible when compared with the color of the blank solution.

3. If selenium is present, it must be completely reduced to the metal with NH_2OH, or it will precipitate when treated with $N_2H_4.H_2O$ and thus obscure the detection of small amounts of tellurium. Heating for 5-6 minutes in a bath of <u>boiling</u> water suffices for the removal of 400 gamma or less of selenium.

4. The small test tubes may be satisfactorily centrifuged in 25 or 50 ml centrifuge cups, and are easily removed with the aid of small forceps. If selenium is present, the solution should be centrifuged for approximately 4-5 minutes.

5. If any turbidity can be observed in the centrifugate by looking down through it against a white background, the tube should be heated in a bath of <u>boiling</u> water for another 4-5 minutes and centrifuged again.

6. The $N_2H_4.H_2O$ should not be added to the hot solution since it would then boil vigorously, due to the large heat of neutralization of the free base; and N_2H_4 would be boiled out of the solution and lost,

7. The black turbidity caused by 4 gamma of tellurium is readily detected (when compared with a blank tube) by looking down through the solution against a white background. It is suggested that the analyst prepare comparison tubes using 4, 10, 20 gamma of tellurium in order to familiarize himself with the yellow color (Note 2) and with the black turbidity caused by these small amounts of tellurium.

P. III-b **<u>Qualitative Test for Arsenic and/or Phosphorus</u>**

This test depends upon the fact that, with molybdic acid, arsenic and phosphoric acids form complex acids which can be reduced to give an intensely blue-colored compound.

If iodine is absent (Note 1), pipet 1 ml of the original Fusion Solution into a 15 ml graduated centrifuge tube. Prepare a blank by adding 1 ml of the blank fusion solution to another 15 ml graduated centrifuge tube. (Treat this blank, which serves as a comparison solution, by the following procedure <u>before</u> treating the sample solution, in order to be sure that the reagents introduce no silica or impurities of arsenic or phosphorus into the sample solution.) Add to

centrifuge tube 1 drop of 0.2% phenolphthalein indicator and add 9 F $HClO_4$ dropwise until the solution loses its red color; then add 3 F NaOH dropwise until the solution again becomes red. Finally discharge the red color by adding 1 F $HClO_4$ dropwise (Note 2).

Pipet 1.8 ml of 3 F H_2SO_4 (Note 3) into the centrifuge tube and stir the solution thoroughly (Note 4). Add 2 ml of 0.1 F Na_2MoO_4 (Note 5) with constant stirring; and then, while stirring, dilute the solution to 10 ml with water. Finally add 0.2 ml of 0.5 F $N_2H_4.HClO_4$, and stir the solution thoroughly. Let it stand for 4-5 minutes. Compare the color of the solution with that of the blank (Note 6). (Light blue to dark blue color: presence of arsenic and/or phosphorus. Note 7.)

Notes.

1. A preliminary treatment is necessary in order to remove iodine before the test can be made. Iodine in large amount would otherwise cause a color indicating the presence of arsenic and/or phosphorus. If iodine is present, proceed as follows:

> Pipet 1 ml of the original Fusion Solution into a 10 ml beaker. (Prepare a blank by adding 1 ml of the blank fusion solution to another 10 ml beaker. Treat the blank, which serves as a comparison solution, by the following procedure before treating the sample solution, in order to assure that the reagents introduce no silica or impurities of arsenic or phosphorus into the sample solution.) Add to the solution 0.5 ml of 16 F HNO_3, and 1 drop of 1 F $NaNO_2$. Evaporate the solution with constant swirling over a free flame until the volume is about 0.5 ml, or further, until the solution is no longer yellow. Transfer the solution from the beaker to a 15 ml graduated centrifuge tube; use 1 ml of water as wash solution. Add 1 drop of 0.2% phenolphthalein indicator, and add 3 F NaOH dropwise until the solution becomes pink. Then decolorize the solution by adding 1 F $HClO_4$ dropwise. Treat this solution as directed in the last paragraph, beginning with the addition of H_2SO_4.

Chromium interferes with the test by requiring the addition of an excessive amount of $N_2H_4.HClO_4$. However, this test is only performed when the Arsenic Group precipitate is white and therefore only when chromium is absent. If it is desired to make this test when chromium is present or may be present, proceed as directed in this note above; by that treatment, chromate ion will be reduced to chromic ion and the test can be made satisfactorily.

2. The following elements, if present, may precipitate completely or partially from the solution as phosphates, arsenates, hydrated oxides, or hydroxides: dipositive copper, dipositive lead, dipositive cadmium, dipositive zinc, (dipositive cobalt), tetrapositive tin, (and aluminum). If any precipitate is present at this point, it should be left in the solution, as it may contain arsenic or phosphorus.

3. It is important to adjust the acid concentration carefully. An acid concentration which is too high represses the production of the blue color from small amounts of arsenic or phosphorus. An acid concentration which is too low may allow any silica to react with the Na_2MoO_4 giving a blue color and thus interfering with the test.

4. A white turbidity indicates the presence of silica or lead sulfate. If the mixture is turbid, proceed as follows:

Centrifuge the solution until it is clear and transfer the centrifugate to a 15 ml centrifuge tube. Discard the precipitate.

5. The 0.1 F Na_2MoO_4 solution should be reasonable freshly prepared and must be contained in a paraffined bottle in order to keep the solution silica-free.

6. A colored blank indicates that silica is likely to be present in the 0.1 F Na_2MoO_4. In the event that the blank is not colorless after standing 5 minutes, a fresh solution of Na_2MoO_4 should be prepared; the blank should develop no color within 5 minutes.

7. Four gamma of phosphorus or of arsenic can be detected easily by this test. When small amounts of arsenic are present (4-10 gamma in the 1 ml portion of the Fusion Solution), the full development of the blue color requires about 2-5 minutes. The development of the color with small amounts of phosphorus is rapid.

A comparison solution containing enough NaH_2AsO_4 test solution to provide 4-10 gamma of arsenic should be treated by the procedure and used as a comparison if the sample test is doubtful.

P. III-c

Qualitative Test for Arsenic

This test is a modification of the well-known Gutzeit test for arsenic. The arsenic is reduced to arsine by tin in a hydrochloric acid solution and the arsine is detected by the stain produced when it reacts with mercuric chloride paper.

Pipet 1 ml of the Fusion Solution into a 15 ml ground glass stoppered centrifuge tube. Add 1 ml of 12 F HCl dropwise and then add 0.5 g of granulated tin (Note 1). Roll some glass wool into a compact ball the size of a pea and insert it into the male joint of the outlet tube of the generator (see Fig. 11). The outlet tube should be dry. Moisten the plug of glass wool with 2 drops of saturated $Pb(C_2H_3O_2)_2$ solution (Note 2). Insert a strip of mercuric chloride test paper through the constriction of the outlet tube so that the lower edge of the paper extends 6-8 mm into the tube (Note 3). Connect the two pieces of apparatus as shown in Fig. 11, making sure that the joint fits tightly (Note 4). Place the tip of the centrifuge tube in a glycerine or dibutyl-phthalate bath at 120-140° C so that the level of the bath liquid is just

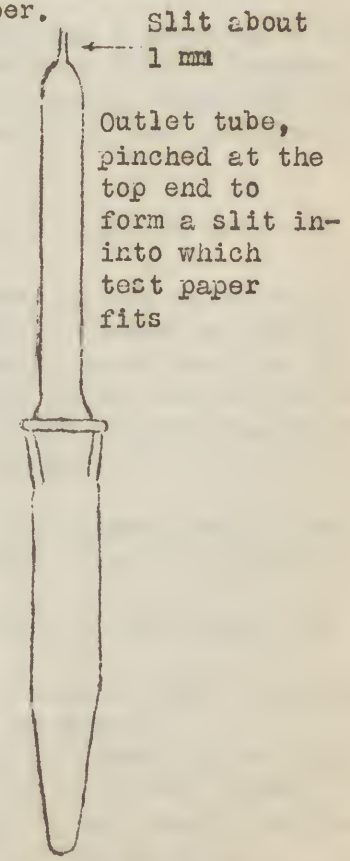


Figure 11. Arsine Generator
A 15 ml graduated centrifuge tube (with a female 14/20 joint) fitted with a male 14/20 joint attached to 11 mm tubing.

above the level of the metallic tin in the tube (Notes 5 and 6). Heat the mixture for 5 minutes after a vigorous evolution of hydrogen has begun. If a color appears on the paper, immediately force the paper about 2 cm further into the tube, and then heat the mixture for 3-4 minutes longer (Note 7). (Yellow, orange, or brown color on the mercuric chloride test paper: presence of arsenic. Note 3.)

Notes.

1. A portion from each new supply of the tin should be put through this procedure to insure that no significant amount of arsenic is present in this reagent. Reagent grade, arsenic-free, granulated tin of about 30 mesh should be used. If arsenic is found in the tin, and if no better tin is available, a blank test should be made with every test of the Fusion Solution. This blank test is made by adding 1 ml of the blank fusion solution to a glass stoppered centrifuge tube and treating it by the same procedure used for the Fusion Solution.

Tin is used instead of zinc (as in the conventional Gutzeit reduction) in order to eliminate interference from any antimony originally present in the Fusion Solution.

2. The interference by H_2S from any sulfur in the sample is prevented by passing the gases past a $Pb(C_2H_3O_2)_2$ solution. If H_2S is present, black PbS forms on the glass wool.

3. The sensitivity of the mercuric chloride test paper (prepared as directed in Appendix I) should be tested every 4-8 months. Make this test as follows:

> Add an amount of Na_2HAsO_4 test solution containing 4 gamma of arsenic to 1 ml of water in a ground-glass stoppered centrifuge tube. Prepare a blank by adding 1 ml of water to a ground-glass stoppered centrifuge tube. Treat the two solutions by this procedure beginning with the addition of HCl in the first paragraph.

If the test paper is satisfactory, a yellow color, as compared with the color on the blank paper, will appear.

4. Any granules of tin between the ground glass surfaces of the joint will prevent the surfaces from forming a tight seal, and all arsine formed may escape.

5. A high bath temperature is maintained to provide ample local heating of the tin and thus cause vigorous hydrogen evolution. The bath liquid should not be more than 2-3 mm above the level of the metal in the tube or the aqueous solution will boil and moisture will condense around and on the test paper; this would result in an uneven stain.

6. If selenium is present, a red precipitate of metallic selenium will form in the solution during the heating. If tellurium is present, a black precipitate of metallic tellurium will form.

7. If arsenic is present, the first color usually appears on the paper 2-3 minutes after vigorous evolution of hydrogen has begun.

8. Four gamma of arsenic produce a yellow color on the paper. With increasing amounts of arsenic, the color varies through reddish-orange to brown.

A rough estimation of the amount of arsenic can be made by comparing the paper with strips which represent, say, 10, 20, 50, and 100 gamma of arsenic. These strips can be preserved under transparent cellulose tape. From the length and intensity of the stain the amount of arsenic can be estimated to within 40%.

P. III-d Qualitative Test for Phosphorus

This test utilizes the yellow color of molybdophosphoric acid for the detection of small amounts of phosphorus; large quantities produce the yellow ammonium molybdophosphate precipitate.

If iodine and chromium have been found absent, and if a glass capsule has not been used to contain the sample during fusion (Note 1), pipet 1 ml of the Fusion Solution into a 15 ml graduated centrifuge tube. Prepare a blank by pipetting 1 ml of the blank fusion solution into another centrifuge tube. (Treat this blank, which serves as a comparison solution, by the following procedure before treating the sample solution, in order to be sure that the reagents used in this procedure do not introduce interfering amounts of impurities. Note 2.)

Add 0.6 ml of 16 F HNO_3, mix well, and cool the solution with tap water (Note 3). Add to the centrifuge tube 0.4 ml of 1.5 F ammonium molybdate reagent (Note 4) dropwise, stirring after the addition of each drop until any local precipitate dissolves (Note 5). Let the solution stand 2-5 minutes (Note 6). (Yellow solution or yellow precipitate: presence of phosphorus. Note 7.) Compare the color with that of the blank (Note 8).

Notes.

1. A preliminary treatment, provided in this note, is necessary in order to remove iodide, chromate, and silicate before the test is made.

Iodide, if not removed, would be oxidized to iodine by the HNO_3 and would mask the test color. In this preliminary treatment, iodide is oxidized to iodine by nitrite and removed by boiling.

Chromate would interfere because it is colored. In this preliminary treatment, chromate is reduced to chromic ion. If the 1 ml portion of the Fusion Solution contains more than about 150 gamma of chromium as chromate, the blue-green color of the chromic ion will interfere with the detection of amounts of phosphorus less than 10 gamma. The detection of amounts of phosphorus greater than 10 gamma is possible in these cases because of the appearance of the yellow precipitate of ammonium molybdophosphate (see Note 7).

More than 400 gamma of silicon as silicate in the 1 ml portion will interfere with this test by finally causing a yellow color similar to the test color. It is very unlikely that this much silica will come from the sample itself. In this preliminary treatment, silica is precipitated out and discarded.

Therefore, if iodine or chromium is present, or if a glass capsule has been used to contain the sample during fusion, proceed as follows:

Pipet 1 ml of the Fusion Solution into a 25 ml beaker. (Prepare a blank by adding 1 ml of the blank fusion solution into another beaker. Treat this blank, which serves as a comparison solution, by the following procedure before the sample solution, in order to be sure that the reagents used in P. I and in this procedure do not introduce interfering amounts of impurities. Note 2.) Add 1 ml of 12 F HCl and 0.1 ml of 1 F $NaNO_2$. While keeping the beaker in constant motion so that excessive spattering does not occur, evaporate the solution to 0.1-0.2 ml over a free flame. Thoroughly mix the residue in the beaker with 1 ml of water and transfer the solution to a 15 ml centrifuge tube.

If a precipitate (silica) is present, centrifuge the mixture and transfer the centrifugate to another 15 ml centrifuge tube. Discard the precipitate.

Treat the solution by the above procedure, (P. III-d), beginning with the addition of HNO_3.

2. The blank test is made before the sample test so that, if the ammonium molybdate reagent contains silica (see Note 4), the reagent will not be added to the sample solution, but will be discarded and replaced by fresh reagent. Therefore, if the blank test is positive, prepare a fresh solution of ammonium molybdate reagent and repeat the blank test.

3. If the solution is not cool, and if arsenic is present, a yellow molybdoarsenate compound will form and interfere with the test for phosphorus.

4. The ammonium molybdate reagent is capable of dissolving silica from glass and can thus give a positive test for phosphorus even when phosphorus is absent. (The reagent should be stored in a paraffined bottle; however, even then it may contain silica due to flaws in the paraffin lining.)

5. The ammonium molybdate reagent must be added dropwise, with stirring; otherwise, as little as 100 gamma of silicon as silica will give a yellow color similar to the test color.

The white precipitate which forms on the addition of the ammonium molybdate is molybdic acid; it dissolves when the mixture is stirred.

6. The yellow color is slow to appear for amounts of phosphorus less than 10 gamma, but immediate for larger amounts.

7. A yellow color will be obtained if the amount of phosphorus in the solution being tested is less than 10 gamma; a precipitate will form if a larger amount is present. Small amounts may also begin to precipitate in 5-10 minutes, so that a confirmatory detection may be made by centrifuging the solution and observing the yellow precipitate.

Four gamma of phosphorus, present as phosphate, are readily detected by this procedure. Even large amounts (100-400 gamma) of arsenate and silicate, the principal interfering constituents, do not give a positive test under the conditions of this procedure.

8. The qualitative test for phosphorus in the blank fusion solution may be weakly positive due to phosphate impurities in the reagents (see Note 20, P. I) or to silica present in the ammonium molybdate reagent (see Note 2). If the test for phosphorus in the sample solution is no more definite than that in the blank, phosphorus can be assumed to be absent from the sample.

P. III-1 Removal of Silver and Detection of Chromium

In this procedure the precipitates of Ag_2CrO_4, $Ag_2H_4TeO_6$, Ag_3AsO_4, and Ag_3PO_4 are dissolved in acid and the silver is removed by precipitating AgCl.

Add 0.2 ml of 9 F $HClO_4$ dropwise, and with stirring, to the precipitate

from P. III. Add 2.5 ml of water in such a way that all of the solution on the wall of the tube is washed to the bottom. Stir the mixture. Note any turbidity (Note 1). Add 0.1 ml of 6 F HCl and stir vigorously for 2-3 minutes (Note 2). Centrifuge the mixture. (Yellow or orange color in the centrifugate: presence of chromium. Note 3.) Add 1 drop of 6 F HCl to the clear centrifugate; if additional precipitate forms, centrifuge it out. Treat the mixture by Option A, B, C, or D below.

Option A. If chromium, tellurium, and arsenic are absent, and phosphorus is present, transfer the centrifugate to a 15 ml graduated centrifuge tube. Wash the residue with two 0.5 ml portions of water, each containing 3 drops of 6 F HCl, and combine the wash solution with the centrifugate. Treat the centrifugate by P. III-7. Discard the residue (Note 4).

Option B. If both chromium and tellurium are absent, but arsenic (or arsenic and phosphorus) is present, transfer the centrifugate to a 50 ml ground-glass stoppered flask. Wash the residue with two 0.5 ml portions of water, each containing 3 drops of 6 F HCl, and combine the wash solution with the centrifugate. Add 4 ml of 12 F HCl to the centrifugate and treat it by P. III-4. Discard the residue (Note 4).

Option C. If chromium is absent and tellurium is present, transfer the centrifugate to a 15 ml ground-glass stoppered graduated centrifuge tube. Wash the residue with two 0.5 ml portions of water, each containing 3 drops of 6 F HCl, and combine the wash solution with the centrifugate. Treat the centrifugate by P. III-3. Discard the residue (Note 4).

Option D. If chromium is present, or may be present (Note 3), transfer the centrifugate obtained in the first paragraph of this procedure to a 15 ml graduated centrifuge tube. Wash the residue with two 0.5 ml portions of water, each containing 1 drop of 6 F HCl, and combine the wash solution with the centrifugate. Discard the residue if it is white (Note 5). Add 6 F NaOH dropwise to the centrifugate until the solution has a pH of 4-7 (approximately 0.4 ml will be required), and then add 0.2 ml excess (Note 6). If the solution is not clear, centrifuge it. (Blue precipitate: presence of copper. Yellow or orange color in the centrifugate:

presence of chromium.) Without separating the solution from any precipitate, treat the mixture by P. III-2.

Notes.

1. If this solution is clear, or if only a small amount of black precipitate (metallic silver) is present, interfering amounts (see Notes 4 and 5) of tin or lead or certain other metallic elements are absent. In this case, the procedure described in Note 4 can be omitted.

2. The 9 F $HClO_4$ is added in order to dissolve most of the precipitate before the addition of 6 F HCl. When HCl is added all of the silver present is precipitated as AgCl. It is imperative that the precipitate be thoroughly agitated for 2-3 minutes after adding the 6 F HCl so that no tellurate, phosphate, or arsenate remains inclosed in a coating of silver chloride. All lumps should be broken into small flakes.

3. If as much as 40 gamma of chromium are present, the centrifugate will be distinctly yellow.

In the presence of certain metallic elements such as lead, chromium (as chromate) will remain in the silver chloride residue, and thus color it yellow. Therefore, if the precipitate is yellow, treat the mixture by Option D of this procedure.

Large amounts of copper (more than 1 mg) will impart a bluish color to the solution and may obscure small amounts of chromium; in this case, treat the solution by Option D of this procedure.

4. If tin is present, arsenate or phosphate may be in this residue. If tin is likely to be present, proceed as follows:

> Wash the silver chloride residue with two successive 0.5 ml portions of NaOH wash solution prepared by adding 0.2 ml of 6 F NaOH to 1 ml of wash water. Add these washings to the centrifugate obtained from Option A, B, C, or D of this procedure. Discard the residue.

5. In the presence of certain metallic elements such as lead, chromium (as chromate) will remain in the silver chloride residue, and thus color it yellow. In this case, or if tin is likely to be present, treat the silver chloride residue by Note 4.

6. Cupric ion, if not removed, would interfere with the colorimetric estimation of chromium because it forms a yellow colored complex anion ($CuCl_4^{=}$) with hydrochloric acid. Copper is completely precipitated here as $Cu(OH)_2$ by the NaOH. Since no positive information about the presence of small amounts of copper can be obtained from the System of Analysis for the Acidic Elements, NaOH is always added. Since this precipitate may also contain CuH_4TeO_6, $Cu_3(AsO_4)_2$, or $Cu_3(PO_4)_2$, the $Cu(OH)_2$ precipitate will be dissolved in HCl and added to the solution again after the estimation of chromium. Provision for this is made in Notes 10 and 11, P. III-2.

P. III-2 Estimation of Chromium

> In this procedure the solution is made 4 F in hydrochloric acid and the intensity of the dichromate color is measured with a colorimeter.

If chromium is present, place a blue filter in a colorimeter and adjust the instrument to read zero with a blank solution of 4 F HCl (Notes 1, 2, and 3). Empty the tube and allow it to drain.

If the solution from Option D of P. III-1 contains no precipitate (Note 4), transfer it to the colorimeter tube used to set the instrument to zero. Wash the centrifuge tube with 0.5 ml of water and add the washing to the solution in the colorimeter tube (Note 5).

Pipet into the colorimeter tube 3.3 ml of 12 F HCl and dilute the solution with water to the 10 ml mark (Note 6). Mix the solution well. Place the colorimeter tube in the colorimeter and make the scale reading of the instrument (Note 7). From the calibration graph calculate the percent of chromium in the sample (Notes 8 and 9). Treat the solution by Option A,B, or C below.

Option A. If tellurium is present, transfer the solution from the colorimeter tube to a 15 ml ground-glass stoppered centrifuge tube (Note 10); wash the tube with 1 ml of 4 F HCl. Add the washing to the solution in the centrifuge tube, and treat the solution by P. III-3.

Option B. If tellurium is absent, but arsenic (or arsenic and phosphorus) is present, transfer the solution from the colorimeter tube to a 30 ml centrifuge tube (Note 11). Wash the colorimeter tube with 4 ml of 12 F HCl and add the washing to the solution. Treat the solution by P. III-5.

Option C. If tellurium and arsenic are absent, but phosphorus is present, transfer the solution to a 50 ml conical flask (Note 11). Wash the colorimeter tube with 1 ml of water and add the washing to the solution. Treat the solution by P. III-7.

Notes.

1. See Operation 7, Appendix V regarding the use of the colorimeter.
2. A blue filter should be used with the colorimeter for this estimation. The blank solution for this colorimetric estimation if 4 F HCl.
3. Colorimeter tubes differ appreciably in their wall thicknesses and in their inner diameters. The same tube that is used to contain the blank solution during the adjustment of the instrument to zero reading must be used to contain the solution being analyzed. Moreover, the tube should be placed in the instrument in the same way; e.g., so that the letter "l" of "ml" always faces front.
4. If copper was present, it was precipitated as $Cu(OH)_2$ in P. III-1 (see Note 6, P. III-1). In this case the mixture will contain a precipitate and should be treated as follows:

Transfer the clear centrifugate to the colorimeter tube used to set the colorimeter to zero (Note 5). Wash the precipitate with 1 ml of 0.1 F NaOH. Add the washing to the colorimeter tube and treat the solution by the second and subsequent paragraphs of this procedure. Reserve the precipitate for treatment by Note 10 or Note 11 of this procedure.

5. If a metallic chromate residue was obtained in P. II (see Note 6. P. II), treat that precipitate as follows:

Add 0.5 ml of water and 3 drops of 6 F HCl. Stir and warm the mixture and centrifuge it. Remove the centrifugate with a dropper and add it to the solution in the colorimeter tube. Discard any residue remaining.

6. The HCl concentration is kept at about 4 F since this concentration is required for the possible subsequent reduction of tellurium with NH_2OH.

7. Readings should be made immediately since chromate is slowly reduced to chromic ion by strong HCl solutions. The color in 4 F HCl is stable for at least 5 minutes; after 10-15 minutes the color intensity may have decreased by as much as 3-4%.

8. The procedure to be used in constructing the calibration graph is as follows:

Pipet the desired quantity of K_2CrO_4 test solution into the colorimeter tube used to set the instrument to zero. Add 4-5 ml of water. Pipet 3.3 ml of 12 F HCl into the tube. Dilute to the 10 ml mark with water. Mix the solution well. Place the tube in the colorimeter and observe the scale reading.

It is suggested that the following amounts of chromium be used in the preparation of the graph: 50, 100, 200, 300, 500, 1000, 2000, and 3000 gamma. Further, it is suggested that the data be plotted on two separate sheets of coordinate paper, one of which shows the colorimeter readings of amounts of chromium from 0 to 500 gamma, and the other from 0 to 3000 gamma. Plot the colorimeter readings as ordinates against chromium content (as gamma of chromium) as abscissae.

If nitrogen was present in the sample, this estimation of chromium is probably low due to:
(a) the formation of nitrite during fusion and (b) the reduction of dichromate by nitrite in the acid solution in P. II. The estimation of chromium by P. XIII-1 is not affected by nitrogen from the sample.

As much as 4 mg of tellurate, arsenate, or phosphate do not interfere with this estimation of chromium. Four mg of vanadium give a yellow color corresponding to 0.25 mg of chromium.

10. If a $Cu(OH)_2$ precipitate was reserved (Note 4), and tellurium is present, proceed as follows:

Add to the $Cu(OH)_2$ precipitate 1 ml of 4 F HCl. Stir the mixture until the precipitate has dissolved; then, by means of a dropper, remove the solution and rinse the walls of the empty colorimeter tube with it, and finally add it to the main solution in the 15 ml ground-glass stoppered centrifuge tube. Treat the solution by P. III-3.

11. If a $Cu(OH)_2$ precipitate was reserved (Note 4) and tellurium is absent, proceed as follows:

Add to the $Cu(OH)_2$ precipitate 1 ml of 4 F HCl. Stir the mixture until the precipitate has dissolved; then, by means of a dropper, remove the solution and wash the walls of the empty colorimeter tube with it, and finally add it to the main solution in the 30 ml centrifuge tube or in the 50 ml ground-glass stoppered flask. Treat the solution by P. III-5 if arsenic (or arsenic and phosphorus) is present; or treat the solution by P. III-7 if only phosphorus is present.

In this procedure, tellurate ion is reduced to tellurium metal by hydrazine inaa solution 4 F in hydrochloric acid.

If the colorimetric estimation of chromium was not done, dilute the solution from Option C of P. III-1 with water to 7.3 ml. (This solution should be contained in a 15 ml ground-glass stoppered centrifuge tube.) (Notes 1 and 2.) Add 3.7 ml of 12 F HCl. Treat the solution by the second paragraph below, beginning with the addition of $N_2H_4.H_2O$.

If the colorimetric estimation of chromium was done, treat the solution from Option A of P. III-2, contained in a 15 ml ground-glass stoppered centrifuge tube, by the next paragraph.

Add to the solution 4 drops of 85% $N_2H_4.H_2O$ and mix well. Heat the solution in a bath of boiling water for 15 minutes. (Grey turbidity or precipitate: presence of tellurium. Note 3.) Cool the solution to room temperature and centrifuge it until it is clear. Treat the mixture by Option A, B, or C below.

Option A. If arsenic and phosphorus are absent, discard the centrifugate. Wash the precipitate twice, using 5 drops of 6 F HCl and 10 drops of water each time, added so as to wash the sides of the tubes thoroughly. Discard the washings. Treat the precipitate by P. XIX-1 (Note 4).

Option B. If arsenic (or arsenic and phosphorus) is present, transfer the centrifugate with a dropper to a 30 ml centrifuge tube. Wash the precipitate twice, using 5 drops of 6 F HCl and 10 drops of water each time, added so as to wash the sides of the tube thoroughly. Add the washings to the centrifugate. Treat the precipitate by P. XIX-1 (Note 4). Add to the centrifugate 4 ml of 12 F HCl. Treat the solution by P. III-5.

Option C. If arsenic is absent but phosphorus is present, transfer the centrifugate with a dropper to a 50 ml conical flask. Wash the precipitate twice, using 5 drops of 6 F HCl and 10 drops of water each time, added so as to wash the sides of the tube thoroughly. Add the washings to the centrifugate. Treat the precipitate by P. XIX-1 (Note 4). Treat the centrifugate by P. III-7.

Notes.

1. In order that the reduction of tellurium to the metal will be complete in the time allowed in this procedure it is necessary that the solution be 4 formal in hydrogen ion and 4 formal in chloride ion within narrow limits. For this reason, the directions given in this procedure regarding volumes must be rigorously observed.

2. If a metallic chromate residue was obtained in P. II (see Note 6, P. II), treat that precipitate as follows:

> Add 3.7 ml of 12 F HCl. Stir the mixture and centrifuge it. Remove the centrifugate with a dropper and add it to the solution in the ground-glass stoppered centrifuge tube. Discard any residue.

3. Less than 40 gamma of tellurium give an easily visible grey turbidity within five minutes if the solution is heated in boiling water. If tellurium is present, it is necessary to heat the mixture a total of 15 minutes in boiling water in order to obtain complete precipitation.

4. In case the original sample contained a large amount of tellurium, tellurium may be a constituent of the Fusion Residue due to the limited solubility in the Fusion Solution of sodium tellurate and other metallic tellurates. If tellurium is present here and if a Fusion Residue was obtained, the latter must be treated by P. XI and P. XII, of the System of Analysis for the Basic Elements.

Instructions for the Use of P. III-4, P. III-5, and P. III-6

Two methods for the estimation of arsenic are provided; a direct iodometric estimation (P. III-4), and a supplementary estimation which is made by precipitating As_2S_3 (P. III-5) and then oxidizing the As_2S_3 to arsenate and estimating the arsenate iodometrically (P. III-6).

The direct iodometric estimation, P. III-4, is made by allowing arsenate to oxidize iodide to iodine and titrating the iodine with $Na_2S_2O_3$. The presence of hydrazine used in the separation of tellurium interferes with this estimation; therefore, if tellurium was present, this procedure cannot be used. Hexapositive chromium, pentapositive antimony, and dipositive copper oxidize iodide to iodine under the conditions of this procedure; therefore, if these elements are present, this arsenic estimation does not give correct results.

The considerations are incorporated in Tabular Outline III-b and in the following directions:

> Proceed to P. III-4 if chromium and tellurium are absent.
> Proceed to P. III-5 if chromium or tellurium was present.
> Because of possible interference in P. III-4 by antimony and copper, discredit the result of P. III-4 if the amount of arsenic estimated by that procedure is appreciably greater than the amount of arsenic estimated by P. III-5 (see Note 5, P. III-4).

P. III-4 Estimation of Arsenic

In this procedure, arsenic is estimated by allowing arsenate to oxidize iodide to iodine in a solution which is 6 F in hydrochloric acid. The iodine is titrated with $Na_2S_2O_3$ solution.

Using a capillary tube (see Figure 1/), bubble CO_2 through the solution (contained in a flask) from P. III-1 for 2 minutes so as to sweep out the dissolved air (Note 1). Add to the solution in the flask 0.2 g of KI dissolved in 0.5 ml of water (Note 2). Allow the solution to stand 2-3 minutes, then titrate to the disappearance of the iodine color with standard 0.02 F $Na_2S_2O_3$ (Note 3). From the volume of the thiosulfate used, calculate the percent of arsenic in the sample (Notes 4 and 5).

Add to the solution a volume of 12 F HCl equal to the volume of $Na_2S_2O_3$ used in the titration (Note 6). If the volume of the solution is less than 10 ml, transfer it to a 15 ml graduated centrifuge tube; if the volume of the solution is greater than 10 ml, transfer it to a 30 ml graduated centrifuge tube. Wash the flask with two 1 ml portions of 6 F HCl; add the washings to the solution in the centrifuge tube. Treat the solution immediately by P. III-5.

Notes.

1. If a precipitate was reserved in P. II (see Note 6, P. II), treat it as follows:

> Add 1 ml of 6 F HCl. Stir and warm the mixture. Centrifuge and transfer the centrifugate to the solution in the flask. If a residue remains, discard it.

2. A white crystalline precipitate of $KClO_4$ will probably form upon the addition of the KI; a white gelatinous precipitate of silica may also be present. These precipitates do not interfere with the end-point of the titration. After the titration and before proceeding to P. III-5, centrifuge out any precipitate, wash the centrifuge tube and precipitate with two 0.5 ml portions of 6 F HCl, and add the washings to the centrifugate. Discard the precipitate.

3. Because of the high acid concentration, the starch indicator usually used is not satisfactory here. In a solution of this acidity and of this iodide concentration, the iodine itself furnishes a sufficiently sensitive end-point color.

4. One ml of 0.02 F $Na_2S_2O_3$ corresponds to 0.75 mg of arsenic.

An end-point correction should be made by subtracting the volume of $Na_2S_2O_3$ used for a blank from the volume used for the sample solution. Prepare a blank by treating 10-12 ml of 6 F HCl by the procedure, beginning by bubbling CO_2 through the solution.

5. Antimony and copper interfere with this direct estimation of arsenic. (The "System of Analysis for the Acidic Elements" does not furnish knowledge about the presence or absence of antimony or copper. However, the "System of Analysis for the Basic Elements" does.) Therefore, unless copper and antimony are known to be absent, P. III-5 and P. III-6 will always be performed subsequent to this procedure in order either to substantiate or to discredit the result obtained here.

If the two arsenic estimations indicate about the same amount of arsenic, it is probable that copper and antimony are absent. In this case, this procedure (P. III-4) is likely to give a result somewhat more accurate than that given by P. III-6. However, if P. III-6 indicates appreciably less arsenic than this

procedure does, antimony and/or copper is probably present. In this case the estimation provided by P. III-6 can be accepted as correct.

6. This additional HCl is added in order that the solution will be 6 F during the precipitation of As_2S_3 in P. III-5.

P. III-5 Separation of Arsenic

In this procedure, arsenic is separated by precipitating As_2S_3 from a solution 6 F in HCl.

If P. III-4 was performed, add, dropwise, 0.1 F $Na_2S_2O_3$ to the solution until any iodine color disappears (Notes 1 and 2). If P. III-4 has not been performed, add to the solution from Option B of P. III-2, or from Option B of P. III-3, 2 drops of 7 F HI, allow the solution to stand 2-4 minutes, and then add 1 F $Na_2S_2O_3$, dropwise, until no iodine color remains (Notes 2 and 3).

Using a capillary tube, bubble H_2S through the solution for 5 minutes (Note 4). (Yellow precipitate: presence of arsenic. Note 5.) Centrifuge the mixture (Note 6).

If phosphorus is absent, discard the centrifugate. If phosphorus is present, transfer the centrifugate to a 50 ml conical flask and treat it by P. III-7.

Wash the arsenious sulfide precipitate with three 2 ml portions of 6 F HCl added so as to wash down the sides of the centrifuge tube. Add the first portion of the washings to the centrifugate (Note 7).

Notes.

1. The $Na_2S_2O_3$ is added to reduce any iodine formed by air oxidation of the iodide. The iodine would otherwise oxidize some H_2S to sulfur.
2. Avoid adding any more $Na_2S_2O_3$ than is absolutely necessary, since the excess thiosulfate decomposes rapidly in this acid solution to form sulfur (and SO_2). This sulfur is undesirable; however, when only a small amount is present, it does not interfere with the estimation of arsenic or of phosphorus.
3. Since arsenious sulfide is precipitated more rapidly than arsenic sulfide, provision is made for reducing any pentapositive arsenic with iodide. The $Na_2S_2O_3$ is added to reduce the iodine formed; the iodine would otherwise oxidize some H_2S to sulfur.
4. See Operation 6, Appendix V regarding saturating solutions with H_2S.
5. The yellow precipitate of arsenious sulfide may be used as a supplementary detection of arsenic. Forty gamma of arsenic as the sulfide are readily detected. Copper, if present, may be precipitated here as black copper sulfide. Antimony does not precipitate as the sulfide in the 6 F HCl solution.
6. If the solution is still turbid after several minutes of centrifuging, loosely stopper the centrifuge tube and immerse it in a bath of boiling water for 3 minutes. Cool the solution, and finally centrifuge it again.

7. The iodide present with the arsenious sulfide should be removed as thoroughly as possible by washing.

P. III-6 Supplementary Estimation of Arsenic

In this procedure the arsenic in the As_2S_3 precipitate is estimated by oxidizing it to arsenate in an alkaline solution by the addition of bromine. The excess bromine is reduced to bromide by formic acid. An excess of iodide is then added, and the solution is made 6 formal in hydrochloric acid. Under these conditions the iodide completely reduces arsenate to arsenite. The iodine liberated is titrated with $Na_2S_2O_3$ solution.

Add to the precipitate from P. III-5 (Note 1) 1 ml of 6 F NaOH. Heat the mixture in a bath of boiling water and stir until the precipitate has dissolved completely (Note 2). Add saturated bromine water to the hot solution until an excess is present (Note 3); add the bromine water in such a way as to wash down the walls of the centrifuge tube. Heat the mixture in the bath for 2 minutes. Add 3 ml of water, and then add 6 F HCl until a bromine color appears and the solution is acidic (Note 4). Then add 6 F NaOH dropwise until the bromine color is discharged; avoid adding more than 2-3 drops of NaOH in excess (Note 5). Add 2 ml of 6 F HCOOH, in such asway as to wash down the walls of the tube. Heat in a bath of boiling water for 4 minutes (Note 6). Cool the solution. Using a capillary tube, bubble CO_2 through the solution for 2-3 minutes, and stopper the tube. Dissolve 0.2 g of KI in 0.5 ml of water and add it to the solution.

Note the volume of the solution and then bubble CO_2 through an equal volume of 12 F HCl for 2-3 minutes. Add the HCl to the solution in the centrifuge tube, stopper the tube with a rubber stopper, and cool the solution to room temperature with tap water (Note 7). Titrate to the disappearance of the iodine color with standard 0.02 F $Na_2S_2O_3$ (Note 8). From the volume of $Na_2S_2O_3$ used, calculate the percent of arsenic in the original sample (Note 9).

Notes.

1. The precipitate will probably contain sulfur as well as arsenious sulfide (see Note 2, P. III-5). This sulfur dissolves when the NaOH is added, and is oxidized to sulfate when bromine water is added.

2. Arsenious sulfide and sulfur are soluble in the alkaline solution. If copper has precipitated as the black Cu_2S in P. III-5, that precipitate will not

dissolve in the NaOH solution; a convenient separation of arsenic and copper is thus obtained.

Therefore, if a drak precipitate remains after heating the alkaline solution, proceed as follows:

> Centrifuge the mixture and transfer the centrifugate to another 30 ml centrifuge tube. Wash the precipitate and the centrifuge tube with two 2 ml portions of water; add the washings to the centrifugate. Discard the precipitate. Treat the solution by the procedure above beginning with the addition of bromine water.

3. An excess of bromine is indicated by a very pale yellow color in the solution. However, disulfide or polysulfide may color the solution yellow in the absence of an excess of bromine. Therefore, it is suggested that an amount of bromine water be chosen according to the size of the arsenious sulfide precipitate or by the amount of arsenic found by P. III-4.

Volume of precipitate (ml)	Amount of arsenic (mg)	Amount of bromine water to be added (ml)
0.02	0.5	0.5
0.05	1	1
0.10	2	2
0.20	3	3

4. If a bromine color does not appear when the solution has a pH less than three as shown by wide range indicator paper, not enough bromine water has been added. In this case, add NaOH and more bromine water and heat the solution in a bath of boiling water for several minutes, and then proceed, beginning with the addition of HCl.

5. It is necessary that the solution have a pH greater than 7 before the addition of the HCOOH.

6. Formic acid reduces bromine in the hot solution. The solution must be colorless after heating. If it is not, heat it longer.

7. The solution will become warm when 12 F HCl is added to it.

8. Starch indicator should not be added. See Note 3, P. III-4.

9. One ml of 0.02 F $Na_2S_2O_3$ corresponds to 0.75 mg of arsenic. An end-point correction should be applied. See Note 4, P. III-4.

P. III-7 Precipitation of Phosphorus

In this procedure phosphorus is precipitated as $(NH_4)_3PO_4.12MoO_3$ from a solution 2.0-2.5 formal in HNO_3.

If chromium, tellurium, and arsenic were found absent, treat the solution in the centrifuge tube from P. III-1, Option A, as follows: add 1.0 ml of 16 F HNO_3 to the solution in the centrifuge tube. Dilute the solution to 6 ml. Stir the solution and treat it as directed in the last paragraph beginning with the addition of the acidified $(NH_4)_2MoO_4$ reagent (Note 1).

If chromium and/or tellurium and/or arsenic were present (Note 2), treat

the solution from Option C of P. III-2, Option C of P. III-3, or from P. III-5 (Note 3) by this procedure beginning with the next paragraph.

While constantly swirling the flask, boil the solution until the volume has been reduced by half (Note 4); then add 4 ml of 16 F HNO_3 (at first, dropwise) and evaporate to 1.0 ml (Notes 5 and 6). (If the solution is not colorless, repeat the evaporation with another portion of HNO_3.) Cool the mixture. Transfer the mixture with a dropper to a 30 ml graduated centrifuge tube. Dilute the mixture to 1.5 ml with 16 F HNO_3. Wash the flask with water and add the water to the solution; use enough water to make the final volume of solution 9-10 ml.

To 2.0 ml of 1.5 F ammonium molybdate reagent, quickly add 4.0 ml of 6 F HNO_3 and stir until the last particle of precipitate has dissolved (Note 7). Pour this solution into the sample solution in the centrifuge tube. Place the tube in a water bath at 45-55° and stir intermittently for 5 minutes (Notes 8 and 9). (Yellow precipitate: presence of phosphorus.) Add 1 drop of 1% Aerosol OT to the solution; then centrifuge and discard the centrifugate (Note 10). Wash the precipitate with three 1 ml portions of 1 F $NaNO_3$, adding the $NaNO_3$ so as to wash down the walls of the centrifuge tube. Discard the washings (Note 11). Treat the precipitate by P. III-8.

Notes.

1. In case a precipitate of metallic phosphate was obtained in P. II (see Note 6, P. II), treat the precipitate as follows:

> Add 1 ml of 12 F HCl. Boil the mixture with constant stirring, over a free flame or in a glycerine bath (see Operation 4, Appendix V) until the volume is 0.5 ml. Add to the mixture 0.5 ml of 6 F HCl and centrifuge it. Add the centrifugate to the solution in the centrifuge tube. Discard any precipitate.

2. Large amounts of chloride prevent complete precipitation of ammonium molybdophosphate by forming with molybdenum the soluble, unionized $MoO(OH)_2Cl_2$ or MoO_2Cl_2. By the procedure provided, most of the HCl is removed by evaporating the solution with HNO_3.

3. The mixture from P. III-5 may contain a white precipitate of sulfur (see Note 2, P. III-5). Most of this precipitate will dissolve when the mixture is boiled with HNO_3. The remainder will form a small dark lump which does not interfere.

4. When evaporating a solution to a small volume, take care to avoid loss of the concentrated solution through spattering or bumping. The evaporation is best carried out over an open flame, the flask being swirled constantly.

5. Estimate the volume of solution as carefully as possible by using a comparison flask containing just 1 ml of water.

6. If arsenic was present and KI has been added in P. III-4, a precipitate of $KClO_4$ will form. This will dissolve when the solution is subsequently diluted and heated.

If arsenic was absent, a turbidity indicates the presence of silica, stannic phosphate, or hydrous antimony oxide. In case arsenic was absent and the mixture is turbid, proceed as follows:

> Add to the mixture just 1 ml of 6 F HCl and warm. Cool and then transfer the mixture with a dropper to a 15 ml graduated centrifuge tube. Dilute to 2.2 ml with 16 F HNO_3. Wash the flask with 4 ml of water and add the washing to the centrifuge tube. If any residue is present, centrifuge it out and discard it. Treat the clear solution by the last paragraph of this procedure beginning with the addition of the acidified $(NH_4)_2MoO_4$ reagent.

7. When the HNO_3 is first added to the $(NH_4)_2MoO_4$ reagent, a white precipitate of molybdic acid will form. Unless the HNO_3 has been added too slowly, the precipitate will dissolve when the solution is stirred.

8. The temperature regulation is quite important. A water bath should be used for heating the solution. If the mixture is not warm enough, precipitation of the phosphate is incomplete. Too high a temperature, even locally, will cause precipitation of molybdic acid.

9. Since the molybdophosphate precipitate tends to cling to the stirring rod, it is convenient to use the same stirring rod during the precipitation and during the subsequent titration.

10. Unless Aerosol OT is added, a layer of molybdophosphate precipitate forms on the surface of the solution and does not come down when the tube is centrifuged.

11. The precipitate is washed with sodium nitrate solution instead of with water, since molybdic acid is more soluble in salt solutions than in water. The final washing should have a pH of 4-5 as shown by wide-range indicator paper. If it does not, the molybdophosphate precipitate should be washed further with 1 ml portions of 1 F $NaNO_3$.

P. III-8 Estimation of Phosphorus

> In this procedure phosphorus in the $(NH_4)_3PO_4.12MoO_3$ precipitate is estimated by titrating with NaOH solution to a phenolphthalein end-point.

Add to the precipitate from P. III-7 standard 0.1 F NaOH from a 10 ml buret dropwise and with stirring until the precipitate has nearly dissolved (Note 1). While there is still a definite turbidity in the solution, add 1 drop of phenolphthalein indicator; then continue titrating to the pink phenolphthalein end-point. From the volume of NaOH used, calculate the percent of phosphorus in the sample (Notes 2 and 3).

Notes.

1. The amount of 0.1 F NaOH usually required is so large that the use of a micro buret is impractical.

Constant stirring during the titration is necessary to avoid over-running the end-point because the precipitate may be somewhat slow in dissolving. Heating the tube to 40-60° will ensure more rapid solution.

2. In case one or more Alkaline Earth Group elements (Mg, Ba, Sr, or Ca) may have been present in the original sample or were found present by the "System of Analysis for the Basic Elements", and in case phosphorus has been detected in P. III-c or in P. III-6 and P. III-7, an additional amount of phosphorus may have been present in the Fusion Residue, due to a partial precipitation of alkaline earth phosphates from the alkaline Fusion Solution. This amount of phosphorus may constitute a large part (up to 60%) of that present in the sample and should be estimated as directed below. It has been found that enough phosphorus will always pass into the Fusion Solution, even in the presence of a large amount of each of the Alkaline Earth Group elements, to be detected in P. III-c and in P. III-6.

If the Alkaline Earth Group elements have been found absent by P. XVII, omit the following paragraphs of this note.

If the Alkaline Earth Group elements are present, as shown by P. XVII, or may be present, treat an aliquot of the hydrochloric acid solution of the Fusion Residue from P. XI as directed below. (If P. XI has not yet been performed, treat the Fusion Residue by P. XI first.)

> Pipet 4 ml of the hydrochloric acid solution (in case the semi-micro bomb was used in P. I), or 2 ml of the hydrochloric acid solution (in case the micro bomb was used) into a 25 ml conical flask. Evaporate the solution with constant swirling over a free flame to between 0.7 and 1.0 ml. Cool the solution and add to it 1.2 ml of 16 F HNO_3. Transfer the solution to a 15 ml graduated centrifuge tube. Wash the flask with 4 ml of water and add the washing to the solution in the centrifuge tube. Treat the solution by the last paragraph of P. III-7, beginning with the addition of $(NH_4)_2MoO_4$.

3. One ml of 0.1 F NaOH corresponds to 0.135 mg of phosphorus.

If only a small amount (less than 0.3-0.4 mg) of phosphorus is found, and if the qualitative test for phosphorus in the blank fusion solution (see Note 8, P. III-d) indicated that phosphate was present as an impurity in the reagents used in P. I, a 5 ml portion of the blank fusion solution should be analyzed for phosphorus. This is done as follows:

> Pipet 5 ml of the blank fusion solution into a 15 ml centrifuge tube. Carefully neutralize the solution to a pH of 2-5 with 16 F HNO_3 and add 1.7 ml of the acid in excess. Treat the solution by the last paragraph of P. III-7 and by P. III-8.

Remember that only 5 ml of the blank fusion solution were used, whereas the analysis of the sample used 10 ml of Fusion Solution.

Tabular Outline IV

The Analysis for the Sulfur Group Elements

Solution from P. III: $SeO_4^=$, $SO_4^=$, H_3BO_3, Ag^+, HCO_3^-.

P. IV. Add HCl. Boil. Add HBr.

Precipitate: AgCl Discard.	Solution: $HSeO_4^-$, HSO_4^-, H_3BO_3. P. IV-1. Add HBr and $NH_2OH.HCl$.

Precipitate: Se, P. XVIII-1. Add KBr, $KBrO_3$, and HCl. Heat. (H_2SeO_3, Br_2, Br^-, H^+Cl^-) Add HCOOH (H_2SeO_3, Br^-, CO_2, HCOOH, H^+Cl^-) Cool. Add KI. (Se, I_3^-). Titrate with $Na_2S_2O_3$. (Se, I^-, $S_4O_6^=$)	Solution: HSO_4^-, H_3BO_3, $NH_2OH.H^+Cl^-$, H^+Br^-. P. IV-2. Add NaOH and $BaCl_2$. Heat.

Precipitate: $BaSO_4$. P. IV-3. Add 7 F HI and H_3PO_2. Distill into $Cd(NH_3)_4Cl_2$ receiving sol.	Solution: H_3BO_3, $NH_2OH.H^+Cl^-$, Ba^{++}, H^+Br^-. To P. V.
Precipitate in the receiving solution: CdS. Add KI, $KH(IO_3)_2$, and HCl (S, Cd^{++}, I_3^-) Titrate with $Na_2S_2O_3$. (S, I^-, $S_4O_6^=$)	Residual Solution: Discard.

The Analysis for Sulfur by the Optional Metathesis Method

Precipitate: $BaSO_4$ (from P. IV-2).

Optional P. IV-3. Add K_2CO_3 and NaOH. Heat. Add $HC_2H_3O_2$.

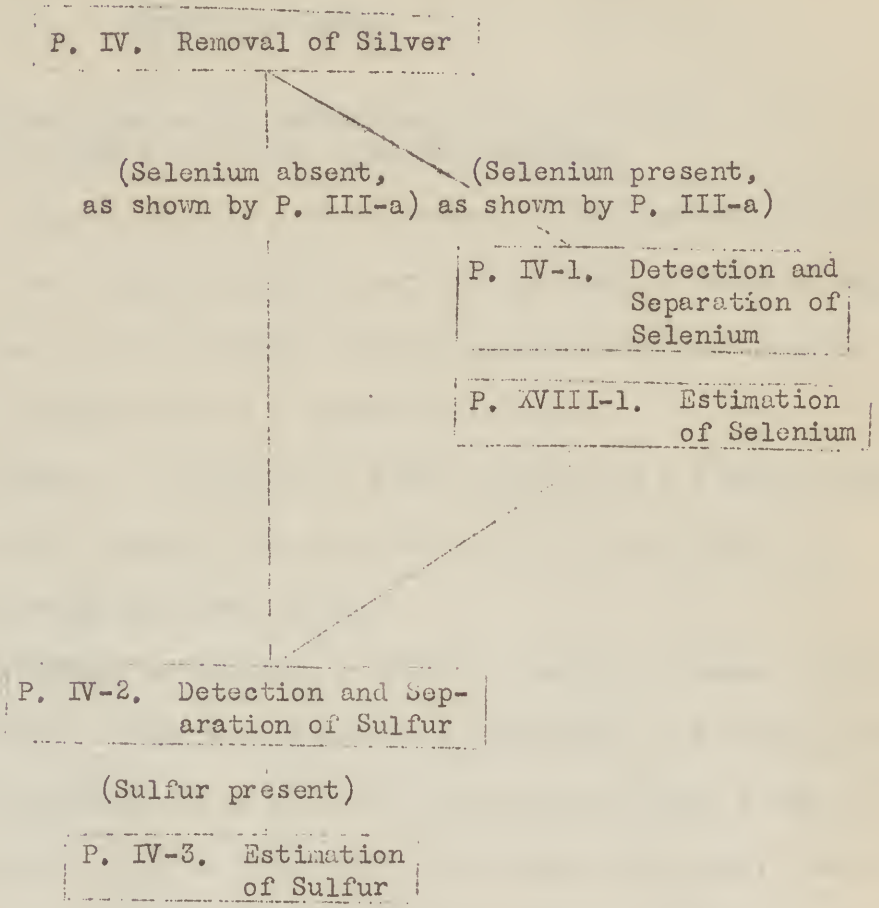
(Ba^{++}, CO_2, $HC_2H_3O_2$)

P. XVII-4 (fourth and subsequent paragraphs). Add K_2CrO_4.

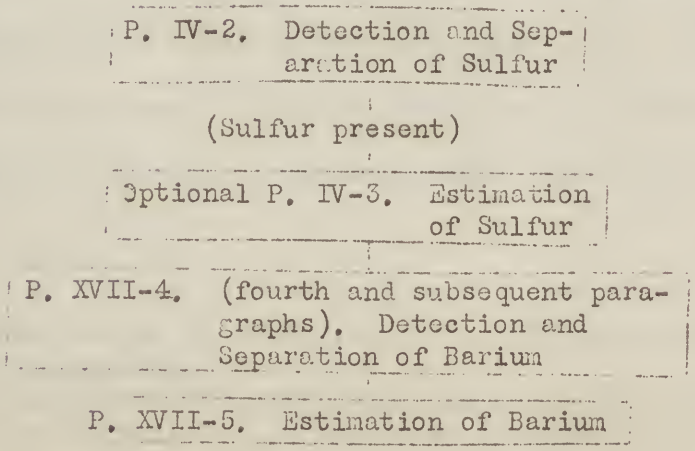
Precipitate: $BaCrO_4$. P. XVII-5. Add HCl. (Ba^{++}, $Cr_2O_7^=$) Add KI. (Ba^{++}, Cr^{+++}, I_3^-, I^-) Titrate with $Na_2S_2O_3$. (Ba^{++}, Cr^{+++}, I^-, $S_4O_6^=$)	Solution: Discard.

Tabular Outline IV-a

Procedure Sequence for the Analysis for the Sulfur Group Elements



Procedure Sequence for the Optional Method for Estimating Sulfur



(Se, S)

P. IV Removal of Silver

In this procedure the silver added in P. II and P. III is precipitated as AgCl and removed from the solution.

To the solution from P. III (in a 50 ml conical flask) add 2-3 drops of 6 F HCl. Add 3 F NaOH to the solution until it has a pH of 8-9, as shown by wide range indicator paper (Note 1); then, while swirling the solution continuously (Note 2), evaporate over an open flame to a volume of 4-5 ml.

If selenium is absent, as shown by P. III-a, slowly add 9 F $HClO_4$ until the solution has a pH of 3-4; then add 0.2 ml of the acid in excess (Note 3). Treat the solution by the second paragraph below.

If selenium is present, as shown by P. III-2, or may be present, slowly neutralize the solution with 9 F HBr to a pH of 3-4, as shown by wide range indicator paper, and pipet into the solution 0.2 ml of the acid in excess (Notes 3 and 4).

Transfer the mixture from the flask to a 15 ml centrifuge tube; use two 0.5 ml portions of water to wash the flask. Centrifuge until the solution is clear. Transfer the solution into a glass stoppered centrifuge tube (see Operations 1 and 2, Appendix V). Wash the precipitate with water and add the washings to the centrifugate; use sufficient wash water to make the volume 7 ml. Discard the residue.

If selenium is absent, treat the solution by P. IV-2.

If selenium is present or may be present, treat the solution by P. IV-1.

Notes.

1. The solution must be made alkaline or significant amounts of H_3BO_3 may be lost during the evaporation.
2. The salt concentration of this solution is so high that bumping or spattering will occur unless the solution in the flask is kept in constant and rapid motion.
3. Silica from reagents or glass capsules (used to contain the sample) may precipitate upon acidification of the solution, and to avoid an unnecessary centrifugation, the silver chloride and silica are removed at the same time. Further, the evaporation of the solution containing the silver chloride coagulates the precipitate and thus expedites the centrifugation.
4. Hydrobromic acid is used because a high bromide ion concentration aids the subsequent reduction of selenate.

P. IV-1 Detection and Separation of Selenium

In this procedure selenate is reduced to selenium metal by hydroxylamine in a solution which is 1.5-1.8 formal in hydrobromic acid.

Pipet into the solution from P. IV 1.0 ml of 9 F HBr, then add 0.3 ml of 5 F $NH_2OH.HCl$. Heat the mixture in a bath of boiling water for 5 minutes. (Red turbidity or precipitate: presence of selenium. Note 1.)

If selenium is absent, add 6 F NaOH to the solution until it has a pH of 4-5, then add 0.2 ml of 9 F $HClO_4$. Treat the solution by P. IV-2.

If selenium is present, heat the mixture for an additional 5 minutes in a bath of boiling water. Cool the solution, and centrifuge until it is clear. Transfer the centrifugate by means of a dropper to a 15 ml glass stoppered centrifuge tube. Wash the selenium metal precipitate with two 0.5 ml portions of water; combine the washings with the centrifugate. Treat the precipitate by P. XVIII-1. Add 6 F NaOH to the centrifugate until it has a pH of 4-5, then add 0.2 ml of 9 F $HClO_4$. Treat this solution by P. IV-2.

Notes.

1. Under the conditions of this procedure 10-20 gamma of selenium are easily visible. The precipitation of larger amounts of selenium will not be complete in the 5 minutes which suffice for its detection. Therefore, another 5 minutes is allowed for the completion of the precipitation of selenium. This time will be sufficient only if the tube is heated in boiling water.

P. IV-2 Detection and Separation of Sulfur

In this procedure sulfate is precipitated from an acid solution as $BaSO_4$.

To the solution, contained in a glass stoppered centrifuge tube, from P. IV or from P. IV-1, add 0.5 ml of 1 F $BaCl_2$, dropwise, with stirring. Heat the mixture in a bath of boiling water for 3 minutes. Stopper the tube and shake it vigorously for 1 minute (Note 1). Cool the mixture to room temperature and again shake. (White precipitate: presence of sulfur. Note 2.)

If sulfur is absent, transfer the solution to a 50 ml flask; use two 1

ml portions of water to wash the centrifuge tube. Treat the solution by P. V.

If sulfur is present, centrifuge the mixture until the solution is clear. Transfer the centrifugate to a 50 ml conical flask. Wash the precipitate and the centrifuge tube with three 1 ml portions of 0.01 F $HClO_4$ (Note 3). Add the first washing to the centrifugate; discard the others. Treat the solution by P. V. Treat the precipitate as soon as possible by P. IV-3 (Note 4).

Notes.

1. When removing the glass stopper, rinse it with several drops of water in such a way that the rinse water collects with the solution.

2. The sensitivity of this detection of sulfur is limited by the presence of appreciable amounts of sulfate in the reagents, especially in any $NH_2OH.HCl$ which may have been used in P. IV-1. The presence of these sulfate impurities makes it necessary to compare the solution being analyzed with a blank made from the reagents before deciding as to the presence of sulfur in the sample. Forty gamma of sulfur can be readily detected under the conditions of the procedure even when as much as 30-50 gamma of sulfur are present because of reagents. In the absence of sulfur from reagents, 5 gamma of sulfur can be readily perceived.

Prepare the blank (which contains one-half quantities of the reagents used in the analysis of the sample) as follows:

> Put 5 ml of the blank fusion solution into a 15 ml glass stoppered centrifuge tube. Add 0.5 ml of 1.5 F Na_2CO_3 and 0.2 ml of 1 F $NaHCO_3$. Add 9 F $HClO_4$ until the pH of the solution is 3-4.
>
> If P. IV-1 was not performed, add 0.1 ml of 9 F $HClO_4$ and treat the solution by P. IV-2, beginning with the addition of $BaCl_2$.
>
> If P. IV-1 was performed, add 0.6 ml of 9 F HBr and 0.15 ml of 5 F $NH_2OH.HCl$. Then add 6 F NaOH until the pH is 4-5. Add 0.1 ml of 9 F $HClO_4$ and treat the solution by P. IV-2, beginning with the addition of $BaCl_2$.

This precipitation of sulfate impurities from the reagents is made using one-half portions of most of the reagents used prior to P. IV-2. Therefore, if the amount of $BaSO_4$ found in the sample solution appears to be less than twice the amount found in this blank solution, sulfur can be assumed to be absent from the sample and the estimation of sulfur can be omitted.

If it is decided that sulfur is present in the sample, and, further, if the amount of sulfur in the blank appears to be significant or if there is not much more sulfur in the sample solution than in the blank solution, the sulfur in the blank should be roughly estimated. This rough estimation is made by comparing the size of the $BaSO_4$ precipitate from the blank with the size of $BaSO_4$ precipitates containing known amounts of sulfur. These latter precipitates are obtained as follows:

> To 7 ml of water add 0.2 ml of 9 F $HClO_4$. Add an appropriate volume of Na_2SO_4 test solution. Add $BaCl_2$ as directed in the procedure.

The amount of sulfur found in the blank should be doubled and subtracted from the amount of sulfur found by the estimation of P. IV-3.

3. Any barium ion that is not removed from the barium sulfate precipitate will form barium carbonate in P. IV-3, and will lead to an erroneously high sulfur estimation.

4. The $BaSO_4$ precipitate should not be allowed to age for longer than one hour.

P. IV-3 Estimation of Sulfur

Two methods for estimating sulfur in the $BaSO_4$ precipitate are provided; the distillation method and the optional metathesis method. The distillation procedure is somewhat shorter, requiring 50-65 minutes as compared to 65-85 minutes required by the other. The optional metathesis involves longer but simpler operations. If the distillation equipment is available and if the analyst has had experience with the procedure, the distillation method is recommended. The two methods are equally accurate.

In the distillation method HI is added to the $BaSO_4$ precipitate and the mixture is heated. Sulfate is reduced to H_2S and this is distilled into a solution containing the $Cd(NH_3)_4^{++}$ ion. The amount of CdS obtained is estimated by allowing it to react with a known amount of iodine and titrating the excess iodine with standard thiosulfate solution.

In the optional metathesis method the $BaSO_4$ precipitate is metathesized to $BaCO_3$. The solution containing the sulfate ion is separated from the precipitate and discarded. The barium in the $BaCO_3$ is then estimated by P. XVII-5. From the amount of barium found, the amount of sulfur in the sample can be calculated.

Distillation Method:

Heat a suitable liquid bath to 145-155° C. (Note 1). To the precipitate from P. IV-1 add 3 ml of colorless 7 F HI (Note 2), and 0.1 ml of 50% H_3PO_2 (Note 3). Thoroughly break up the precipitate with a stirring rod. Fit the centrifuge tube with the distilling apparatus shown in Fig. 12. Immerse the outlet tube in 4 ml of ammoniacal cadmium chloride reagent contained in a 15 ml graduated centrifuge tube. Start a flow of CO_2 through the tubes and adjust it to 1-2 bubbles per second passing from the outlet tube (Note 4). Soon after this, raise

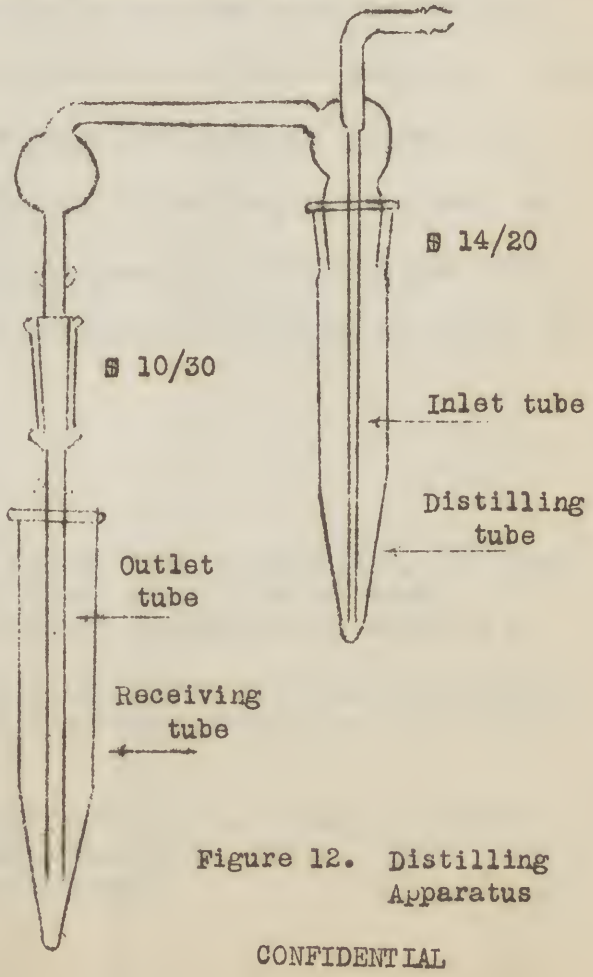


Figure 12. Distilling Apparatus

the bath so that the level of the bath liquid is only slightly above the level of the solution in the tube. Maintaining the bath temperature at 145-155° C, continue the distillation until the solution is clear and then distil for an additional five minutes (Note 5). (Yellow precipitate in the receiving tube: presence of sulfur. Note 6.)

Disconnect the apparatus. Remove from the outlet tube any adhering precipitate with the aid of a stirring rod and 2-6 ml of 15 F NH_4OH; collect the washings in the receiving tube. Centrifuge the mixture in the receiving tube. With the aid of a dropper remove and discard the centrifugate. Wash the precipitate 3-4 times with 2 ml portions of a solution made by adding 2 ml of 6 F $HC_2H_3O_2$ to 1 ml of 6 F NaOH and diluting the solution to 10 ml (Note 7). Discard the washings.

Dissolve 0.1 g of KI in 3 ml of water and add it to the precipitate. Flush out the tube with CO_2. Pipet in an excess of standard 0.004 F $KH(IO_3)_2$ solution (Note 8). Add 1 drop of 6 F HCl and thoroughly stir the mixture. Slowly add sufficient 12 F HCl to make the final acid concentration 3 F (Note 8), and again stir the mixture thoroughly. If not enough $KH(IO_3)_2$ has been added as indicated by no iodine color in the solution, pipet in another ml of 0.004 F $KH(IO_3)_2$. Stopper the tube with a rubber stopper and allow it to stand 1-2 minutes. Titrate with standard 0.02 F $Na_2S_2O_3$ solution until the iodine color becomes faint; then add 5 drops of starch indicator and titrate to the disappearance of the purple color. From the volumes of $Na_2S_2O_3$ and $KH(IO_3)_2$ used, calculate the percent of sulfur in the sample (Note 9).

Notes.

1. A "bakery pan oil" or glycerine bath can be used to advantage. If these are not available, H_2SO_4, dibutylphthalate, or other liquids may be used.
The temperature of the bath is most conveniently controlled by means of a Bunsen burner.

2. Iodine, which may be present in the HI, interferes with this estimation. If the HI is colored, reduce the iodine as follows before adding the acid to the $BaSO_4$ precipitate:

Warm the 7 F HI to 80-100° C. Add 50% H_3PO_2 very slowly dropwise until the solution is colorless. Avoid adding an excess. (Only a few drops should be required.) Cool the solution.

3. The H_3PO_2 prevents the formation of iodine during the reduction of sulfate. During a distillation, some phosphine, PH_3, is formed by the decomposition of H_3PO_2. The PH_3 is distilled into the cadmium receiving solution.

4. The steady rate of flow of CO_2 must be adjusted carefully. If possible, a Kipp generator should be used as the source of CO_2. The Kipp delivers CO_2 at a convenient pressure.

The CO_2 prevents the solution from bumping. If the distillation is continued for an excessive period, a white precipitate of $CdCO_3$ may form in the receiving solution. (Because of this, nitrogen gas can be used advantageously in place of CO_2 if a convenient source is available.)

5. The HI should reflux in the upper part of the distilling tube, without passing in appreciable quantity into the receiving vessel.

6. Twenty-five gamma of sulfur as the yellow CdS can be detected readily.

7. Washing is necessary to remove phosphine, which may be adsorbed on the precipitate and to dissolve $CdCO_3$. If a phosphine odor persists, the washings should be continued until it is eliminated.

8. A known amount of iodine is added to the solution by means of standard $KH(IO_3)_2$ solution. The iodate reacts with the excess of iodide present to form iodine.

The required volume of $KH(IO_3)_2$ can be estimated from the volume of CdS precipitate. One mg of sulfur occupies about 0.05 ml in the centrifuge tube. The following table gives suitable volumes of $KH(IO_3)_2$ to be added. In no case add more than 5 ml. The precipitate may have an abnormally high volume because of the presence of $CdCO_3$.

Estimated Sulfur	Volume of $KH(IO_3)_2$	Volume of 12 F HCl
0.5 mg or less	1 ml	1.4 ml
1 mg	2 ml	1.5 ml
2 mg	3 ml	2.0 ml
3 mg	4 ml	2.0 ml

Enough 12 F HCl is added so that the final acid concentration will be 6 formal. The calculated volumes of HCl to be added are based on the total volume of solution after the addition of $KH(IO_3)_2$. The amount of acid should be measured carefully, as too little acid will cause incomplete solution of sulfide, and too much acid will cause the loss of H_2S.

9. One ml of 0.004 F $KH(IO_3)_2$ corresponds to 0.77 mg of sulfur. One ml of 0.02 F Na_2SO_3 is equivalent to 0.417 ml of 0.004 F $KH(IO_3)_2$.

If the sulfur from the reagents was roughly estimated (see Note 2, P. IV-2), the amount of sulfur found by the estimation should be corrected for the sulfur from the reagents.

Optional Metathesis Method:

To the precipitate from P. IV-2 contained in a glass stoppered centrifuge tube, add 3 ml of a hot (80-100° C.) solution containing equal volumes of 6 F NaOH and 6 F K_2CO_3. Stir the mixture. Heat the centrifuge tube in a bath of boiling water for 10 minutes; remove the tube at 2-3 minute intervals, stopper it, and shake it vigorously for 30-40 seconds (see Note 1, P. IV-2). Cool the mixture to room temperature and again shake. Centrifuge the mixture. With the aid of a dropper, remove the centrifugate and discard it. Wash the residue with two 1 ml portions of a

solution made by adding 0.3 ml of 1.5 F Na_2CO_3 and 0.1 ml of 6 F NaOH to 2 ml of water (Note 1). Discard the washings.

Dissolve the residue in 0.7 ml of 6 F $HC_2H_3O_2$ and add 3 ml of water (Note 2). Add 0.3 ml of 6 F NaOH. Treat the solution by the third and subsequent paragraphs of P. XVII-4, the "Detection and Separation of Barium", and by P. XVII-5, the "Estimation of Barium"; in P. XVII-5, use 0.1 F $Na_2S_2O_3$ instead of 0.02 F $Na_2S_2O_3$ (Note 3).

Notes.

1. If sulfate ion is not completely washed away from the barium carbonate precipitate, barium sulfate will form when the barium carbonate is subsequently dissolved in acetic acid.

2. A slight turbidity may result. If the mixture is quite turbid, the metathesis probably has been incomplete. In this case, proceed as follows:

> Centrifuge the mixture; reserve the centrifugate. Treat the residue with K_2CO_3 and NaOH as directed above; then dissolve the residue in 0.1 ml of 6 F $HC_2H_3O_2$, and add the centrifugate to it. Treat the solution by the remaining parts of this procedure beginning with the addition of NaOH.

3. One ml of 0.1 F $Na_2S_2O_3$ corresponds to 1.07 mg of sulfur.

If the sulfur from the reagents was roughly estimated (see Note 2, P. IV-2), the amount of sulfur found by the estimation should be corrected for the sulfur from the reagents.

Tabular Outlines V and VI

Tabular Outline V

The Analysis for Boron

Solution from P. IV-2: H_3BO_3, H^+Cl^-, Ba^{++}.

P. V. Boil.

(H_3BO_3, Ba^{++}, H^+Cl^-)

Add Methyl red. Adjust pH to 5.5. Add mannitol, $C_6H_8(OH)_6$.

(H^+, $[C_6H_8(OH)_4]_2BO_4^-$, Ba^{++}, Cl^-)

Titrate with NaOH.

($[C_6H_8(OH)_4]_2BO_4^-$, Ba^{++}, Cl^-)

Tabular Outline VI

The Analysis for Fluorine

Fusion Solution: F^-, (other acidic elements, Amphoteric Basic Elements).

P. VI. Add $HClO_4$, $AgNO_3$, and $NaHCO_3$. Heat.

Precipitate:	Solution: F^-.
Arsenic Group.	Add sodium alizarin sulfonate. Adjust pH by adding
Discard.	HCOOH and NaOH. Add 1 drop of 0.001 F $Th(NO_3)_4$.
	(F^-, ThF_4, sodium alizarin sulfonate)

Titrate with $Th(NO_3)_4$.

(ThF_4 and a red lake of alizarin sulfonate or thorium hydroxide.)

P.V Detection and Estimation of Boron

This detection and estimation depends upon the formation of a complex ion of mannitol and borate. The solution is adjusted to a pH of 5.5. All of the boron present is then in the form H_3BO_3. Mannitol is added. The complex ion forms with the simultaneous liberation of hydrogen ion. The solution is titrated with NaOH to a methyl red end-point.

If P.IV-1 has not been performed (Note 1), boil the solution (contained in a 50 ml flask) from P.IV-2 for 30-45 seconds, swirling the flask constantly (Note 2). Stopper the flask and cool the solution to room temperature (Note 3). Prepare a comparison solution by adding 10 ml of water to a 50 ml flask and then adding, by means of pipets, 0.4 ml of 3 F $NH_4C_2H_3O_2$, 0.1 ml of 6 F $HC_2H_3O_2$, and 2 drops of 0.1% methyl orange indicator (Note 4). Add 1 drop of 0.2% methyl red indicator to the sample solution and adjust the pH of the solution, first with 5 F NaOH and then with 0.1 F NaOH (and, if necessary, 0.1 F $HClO_4$), so that its color exactly matches that of the comparison solution. Prepare a blank solution by adding 1 drop of 0.1% methyl red indicator to a volume of water equal to the volume of the sample solution. Add to the blank 0.01 F $HClO_4$ or 0.01 F NaOH until the color of the blank is exactly the same as the color of the comparison solution. Add 0.2 g of solid mannitol to the sample solution and to the blank (Note 5). (Pink or red color in the sample solution more intense than that in the blank: presence of boron. Note 6.)

If boron is absent, discard the solution.

If boron is present, titrate to the color of the comparison solution with standard 0.1 F NaOH. Add 0.4 g more of the mannitol to the solution being titrated. If the pink color reappears, again titrate to the end-point color. Repeat this process until the successive volumes of standard NaOH used to restore the color are approximately equal (within 0.01 ml) after successive additions of 0.4 g portions of mannitol.

Add to the blank the same total amount of mannitol as has been added to the sample solution (Note 7). Titrate the blank with standard 0.1 F NaOH until the end-point color is restored (Note 8). From the volume of NaOH used calculate the

percent of boron in the sample (Note 9).

Notes.

1. If selenium has been removed in P.IV-1, a large amount of NH_2OH has been added to the solution. The procedure in this note provides for removing the NH_2OH by oxidizing it with bromine. The excess bromine is then removed by adding a small amount of $N_2H_4.HClO_4$. If P.IV-1 has been performed, treat the solution (contained in a 50 ml flask) from P.IV-2 as follows:

> Add liquid bromine dropwise and with swirling until the first permanent bromine color is obtained. Then add 0.5 F $N_2H_4.HClO_4$ dropwise and with swirling until the bromine color just disappears. Treat the solution by the procedure above (P.V) beginning with the first sentence.

2. The solution is boiled in order to remove CO_2 which would otherwise interfere with the end-point of the titration.

3. A white turbidity indicates the presence of silica. If the mixture is turbid, remove the silica as described in Note 2, P.II-6, Mercurimetric Method.

4. Both a comparison solution and a blank solution are used in this procedure. The purpose of the comparison solution (which uses methyl orange indicator) is merely to indicate the approximate color of the sample solution and of the blank solution at the end-point. The purpose of the blank solution is to detect and correct for acid impurities in the mannitol.

5. The mannitol should be of the best grade available, and the amount used for the qualitative test should not give any noticeable color change to the blank.

It has been found that the spoon end of a porcelain spatula (120 mm length) is convenient for measuring 0.2 g portions of mannitol.

6. Less than 10 gamma of boron can be readily detected in this way. Because boron may be dissolved from glass the original Fusion Solution should not have been allowed to stand in a glass container for more than several hours prior to analysis (see Note 27, P.I-B).

7. Since the mannitol may contain a trace of acid impurity, the solution may become pink when a large amount of mannitol is added.

8. Usually the blank color is restored on addition of less than 0.1 ml of base.

9. An end-point correction must be made by subtracting the volume of standard NaOH used by the blank from the volume of standard NaOH used by the sample.

One ml of 0.1 F NaOH is equivalent to 1.08 mg of boron.

It is likely that the reagents used in P.I-A and in P.III, and in P.IV-2 (if selenium was present) contain boron. Therefore, if the amount of boron found in the sample is small, an estimation of the amount of boron present in those reagents should be made. The boron from the reagents can be estimated as follows:

> Add 5 ml of the blank fusion solution (which has been stored in a parafinned bottle as described in Note 27, P.I-B) to a 50 ml flask. Add 9 F $HClO_4$ until the solution is acid, then add 0.1 ml more. Add 0.2 ml of 1.5 F Na_2CO_3 and then add 1 F $NaHCO_3$ until the solution has a pH of 6. Add 6 F HCl until the pH is 3-4, and add 0.1 ml in excess.
>
> If P.IV-1 (the "Detection and Separation of Selenium") was performed, add 0.5 ml of 9 F HBr and then add 6 F NaOH until the solution has a pH of 4-5.
>
> Add 0.2 ml of 1 F $BaCl_2$. Treat the solution by the third and subsequent paragraphs of this procedure (P.V).

This estimation of boron is made using one-half portions of most of the reagents used in the procedures prior to P.V. Therefore, the amount of boron found should be doubled in order to obtain the approximate amount of boron present as impurities in the reagents used for the analysis of the sample. CONFIDENTIAL

This procedure is provided as a confirmatory test in case only a small amount of boron is found present by P.V. It also provides a means whereby the analyst can quickly detect boron in the Fusion Solution.

This test depends upon the formation of a red color when curcumin paper which has been moistened with boric acid solution is dried, and upon the formation of a green color when the same dry paper is moistened with NaOH.

Pipet 1 ml of the Fusion Solution (see Note 27, P.I) into a 10 ml beaker. Prepare a blank by adding 1 ml of the blank fusion solution into another 10 ml beaker. Throughout this procedure treat this blank as the sample solution is treated; use the blank as a comparison solution.

Add 6 F HCl dropwise to each of the beakers until the solutions have a pH of 6-7 as shown by wide-range indicator paper. Evaporate the solutions just to dryness, swirling continuously, over a microburner flame. Add to the residues 2 drops of 5 F HCl (Note 1). Stir the mixture. Test the moistened residues with wide-range indicator paper; the pH should be very much less than 2 (Note 2). By means of a stirring rod collect the mixture in one corner of the beaker.

Absorb as much of the solution as possible on a specially prepared strip of curcumin paper (see Appendix I). Dry the paper at 100^{0} C (Notes 3 and 4). (Red or red-orange color on the test paper: presence of boron. Light brown color: absence of boron.)

Add 1 drop of 3 F NaOH to the curcumin test paper. (Green-black color on the test paper: presence of boron. Gray-brown color: absence of boron. Notes 5 and 6.)

Notes.

1. The amount of HCl to be added should be the least amount which allows the moistened residue to be worked easily with a stirring rod. It is desirable to use the least amount since it is then possible to avoid more than one absorption with curcumin paper.

2. The acid concentration of the moistened residue should be between 5 and 6 F. The lowest permissible acid concentration is fixed by the slowness of the development of the test color in solutions of low acid concentrations; The highest acid concentration is fixed by the undesirably high intensity of the blank at high acid concentrations.

If the indicator paper shows a pH greater than 2, add 6 F HCl until the solution has a pH of approximately 2, then add 1 drop of acid in excess.

3. The drying is easily carried out by laying a strip of the test paper on a large watch glass placed on a bath of boiling water.

4. If the curcumin paper will not absorb all of the mixture, it may be necessary to dry the paper and then absorb the remainder of the mixture on it. More than one absorption should be avoided if possible.

5. The green-black test color is a more reliable and more sensitive indication of the presence of boron than the red or red-orange color obtained before this addition of NaOH.

The green-black test color fades to a gray-brown color in 20-30 seconds.

6. A detection of boron is obtained from a solution containing 1-4 gamma of boron per ml. A large amount of chromate (or vanadate) interferes by preventing the test color from appearing.

Significant amounts of boron may be introduced into the Fusion Solution from glassware if the proper precautions are not taken (Notes 15 and 27, P. I). Therefore, consider this fact before making any conclusion as to the presence of boron.

THE ANALYSIS FOR CERTAIN INDIVIDUAL ELEMENTS

(F, N, Si)

P. VI Detection and Estimation of Fluorine

The detection and estimation of fluorine can be made more effectively with a separate portion of the Fusion Solution than with the solution from P. V; this is true principally because of the accumulation of salts and interfering reagents in the latter solution.

This detection and estimation depends upon the insolubility of thorium fluoride and upon the intense red color of a lake of alizarin sulfonate adsorbed on thorium hydroxide. In this procedure thorium is added to a solution whose pH is 3-3.5 and which contains sodium alizarin sulfonate. If fluorine is absent, thorium sodium alizarin sulfonate forms, and a red color is observed. If fluorine is present, thorium fluoride forms and no color is observed.

Pipet 2 ml of the original Fusion Solution into a 15 ml centrifuge tube. Add 9 F $HClO_4$ dropwise until a pH of 3-4 is obtained as shown by wide-range indicator paper.

If all Arsenic Group elements are absent (Note 1), as shown by the analysis of the Arsenic Group, pipet into the solution 0.10 ml of 0.12% sodium alizarin sulfonate indicator (see Appendix I for the preparation of this reagent). If the solution is yellow, add 1 F NaOH dropwise until the solution is red-violet. Add 0.1 F $HClO_4$ until the indicator changes to yellow or light orange; avoid using more than 1 or 2 drops excess of acid. Pipet into the solution 0.12 ml of 3 F NaCOOH and 0.12 ml of 6 F HCOOH, then add 1 drop of 0.001 F $Th(NO_3)_4$. (Pink color: absence of fluorine). If the color is uncertain, add not more than 1 additional drop of the 0.001 F $Th(NO_3)_4$. The change to a pink color will be definite unless fluorine is present (Note 3).

If fluorine is present and the solution is not pink, prepare a comparison solution to be used in the subsequent titration by adding to a 15 ml centrifuge tube 1 ml of water, 3 ml of $Co(NO_3)_2$ test solution containing 1 mg of Co/ml, and, by means of a measuring pipet, 0.02 ml of K_2CrO_4 test solution containing 1 ml of chromium per ml. Titrate the sample solution with standard 0.005 F $Th(NO_3)_4$ until

a pink color matching that of the comparison solution is obtained (Note 4). From the volume of 0.005 F $Th(NO_3)_4$ used calculate the amount of fluorine present (Note 5).

Notes.

1. Phosphate and arsenate interfere with the fluorine detection by forming precipitates with thorium. Both the color and oxidizing action of chromate are objectionable.

Therefore, if any of the Arsenic Group elements is present, or may be present, treat the solution as follows:

> Add 2-3 drops of 1 F $AgNO_3$. Add 1 F $NaHCO_3$ dropwise until a pH of 6.5-7 is obtained as shown by wide range indicator paper (Note 2). Immerse the tube in a bath of boiling water for 2-3 minutes. Centrifuge the mixture until the solution is clear. Transfer the centrifugate with the aid of a dropper to a 15 ml centrifuge tube. Wash the precipitate with 1 ml of water; add the washings to the centrifugate. Treat the solution by the procedure above (P. VI), beginning with the addition of the sodium alizarin sulfonate. Discard the precipitate.

2. A precipitate of Ag_2CrO_4, $Ag_2H_4TeO_6$, Ag_3AsO_4, or Ag_3PO_4 appears as a pH of 6 is approached; the $NaHCO_3$ can be added dropwise up to this point before testing with indicator paper. The final adjustment of the pH should be made as carefully as possible.

3. About 2 drops of 0.001 F $Th(NO_3)_4$ are necessary to produce a pink color when 3 gamma of fluorine are present in the solution being tested. Amounts of fluorine of less than 1-2 gamma in the 2 ml portion are of doubtful significance.

4. When more than about 0.2 mg of fluorine is present in the 2 ml aliquot, a white precipitate of ThF_4 will appear during the titration. When more than about 0.5 mg is present in the aliquot the precipitate changes the appearance of the mixture so much that it is difficult to obtain a match with the clear comparison solution. If more than 0.5 mg of fluorine is present, add a few mg of powdered $CaCO_3$ and 1 more ml of the cobalt test solution to the comparison solution. If enough Fusion Solution is available, an estimation of the fluorine in a 1 ml aliquot ought to be made.

5. An end-point correction must be made by subtracting 0.015 ml from the volume of 0.005 F $Th(NO_3)_4$ used.

One ml of 0.005 F $Th(NO_3)_4$ corresponds to 0.38 mg of fluorine.

P. VII-a Qualitative Test for Nitrogen

> In this test the nitrate and nitrite in the Fusion Solution (Note 1) are reduced to ammonia by Devarda's alloy. Water and ammonia are distilled from the mixture. Ammonia is detected in the distillate by the addition of K_2HgI_4 reagent.

Set up the ammonia distilling apparatus shown in Fig. 13. Use a 100 ml Kjeldahl flask, and use a 15 ml centrifuge tube to collect the distillate. Add 10 ml of water and 0.3 g of Devarda's alloy to the flask. Boil the mixture vigorously until 5 ml of water have been distilled. Discard the distillate (Note 2). Pipet

5 ml of the Fusion Solution into the Kjeldahl flask. Immediately reconnect the flask to the distilling apparatus and heat the Kjeldahl flask with a small flame until 4 ml of liquid have been distilled (Note 3). Reserve the centrifuge tube containing the distillate for treatment by the last paragraph of this procedure.

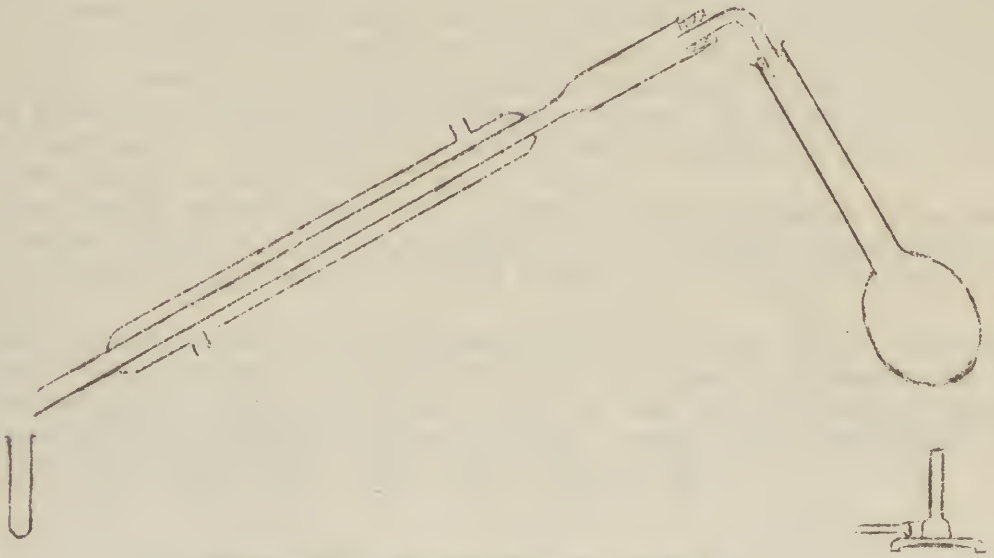


Figure 13. Distilling Apparatus
Micro-burner; Kjeldahl flask (100 ml); No. 2 rubber stopper; right angle bend (120 x 10 mm glass tubing); No. 3 rubber stopper; Liebig condenser (250 mm); and 15 ml centrifuge tube.

Disassemble the apparatus. Rinse the walls of the Kjeldahl flask and the condenser with distilled water. Reassemble the apparatus, using another centrifuge tube to collect the distillate. Prepare a blank distillate as follows: Add 10 ml of water and 0.3 g of Devarda's alloy to the flask. Boil the mixture vigorously until 5 ml of water have been distilled. Discard the distillate. Add 5 ml of the blank fusion solution to the mixture in the flask, reconnect the flask to the distilling apparatus, and heat the flask until 4 ml have been distilled.

Add to each distillate 0.2 ml of K_2HgI_4 reagent. (Orange to red color in the distillate from the Fusion Solution which is more intense than the color in the distillate from the blank fusion solution: presence of nitrogen. Note 4.)

Notes.

1. Nitrogen compounds are converted to nitrate, nitrite, and elementary nitrogen during the fusion.
2. The apparatus is conveniently flushed of any small quantities of ammonia with the steam generated in the Kjeldahl flask during this boiling. Care should be taken to avoid using ammonia as a reagent in the vicinity of the apparatus.

5. The solution may froth extensively if the heating flame is not carefully adjusted. The distillation should require 4-5 minutes.

4. A perceptible orange color will be produced by 1-5 gamma of nitrogen. However, the 5 ml aliquot of the blank fusion solution has been found to contain 10-40 gamma of nitrogen, most of which was present as an impurity in the 30% H_2O_2 used in P. I-B. Blanks may contain even more nitrogen if nitrogen was not carefully flushed from the bomb (see Note 2, P. I-A). Because of the nitrogen in the blank, the detection of small quantities (less than 20 gamma) of sample nitrogen in the aliquot of the Fusion Solution is sometimes difficult. If the "Qualitative Tests for Certain Acidic Elements in Organic Compounds" (Informal Report No. 85) has been performed, the results of the test for nitrogen obtained there should be compared with those obtained here. If either test shows that nitrogen is present, an estimation of nitrogen should be made (P. VII or P. VII-A).

A very approximate estimation of the amount of color produced by various amounts of nitrogen should be made by adding 0.2 ml of K_2HgI_4 reagent to 5 ml of solutions containing varying amounts of 0.03 F $NH_4C_2H_3O_2$ (which contains 0.4 mg of nitrogen per ml).

This method cannot be used for the quantitative estimate of the nitrogen in the sample since a substantial proportion of such nitrogen is converted to elementary nitrogen by the peroxide fusion. The percentage of the total nitrogen found in test analyses of various compounds was as follows: urea, 17; acetanilid, 25; KNO_3, 60; NH_4Cl, 28; $NaNO_2$, 66; CDA, 8-14; and DM, 31.

P. VII Quantitative Determination of Nitrogen

The following procedure does not give quantitative results for esters of nitric acid or for inorganic nitrates. Provision for these compounds is made in P. VII-A. Therefore, P. VII-A should be performed in preference to P. VII if the source of the sample is such that it may contain an ester of nitric acid or an inorganic nitrate. Otherwise, P. VII should be performed, for it is more quickly and easily completed than P. VII-A.

Neither procedure gives quantitative results for inorganic nitrites or for other nitrogen compounds containing readily hydrolyzed nitro groups, nor for compounds containing pyridine nuclei.

In this procedure nitro compounds (azo compounds, hydrazones, and others) are first reduced to amines by hydriodic acid. The amino nitrogen is next converted to ammonium sulfate and distilled into a water receiving solution by the conventional Kjeldahl procedure. The ammonia solution is titrated with standard HCl solution to a methyl red end-point.

Weigh 15-30 mg of the sample (Note 1) into a dry Leiboff urea tube (see Fig. 14) and immediately withdraw the stopper to the closed position.

If the sample in the Leiboff tube is a high boiling liquid which has been weighed ny means of a capillary dropper or pycnometer, or is a solid, proceed to the next paragraph. If the sample is contained in a glass capsule, add 0.1 ml of 50% H_3PO_2 and 1 ml of colorless 7 F HI (Note 2) to the tube and cool the tube in an ice-hydrochloric acid bath (Note 3). Crush the glass capsule by carefully

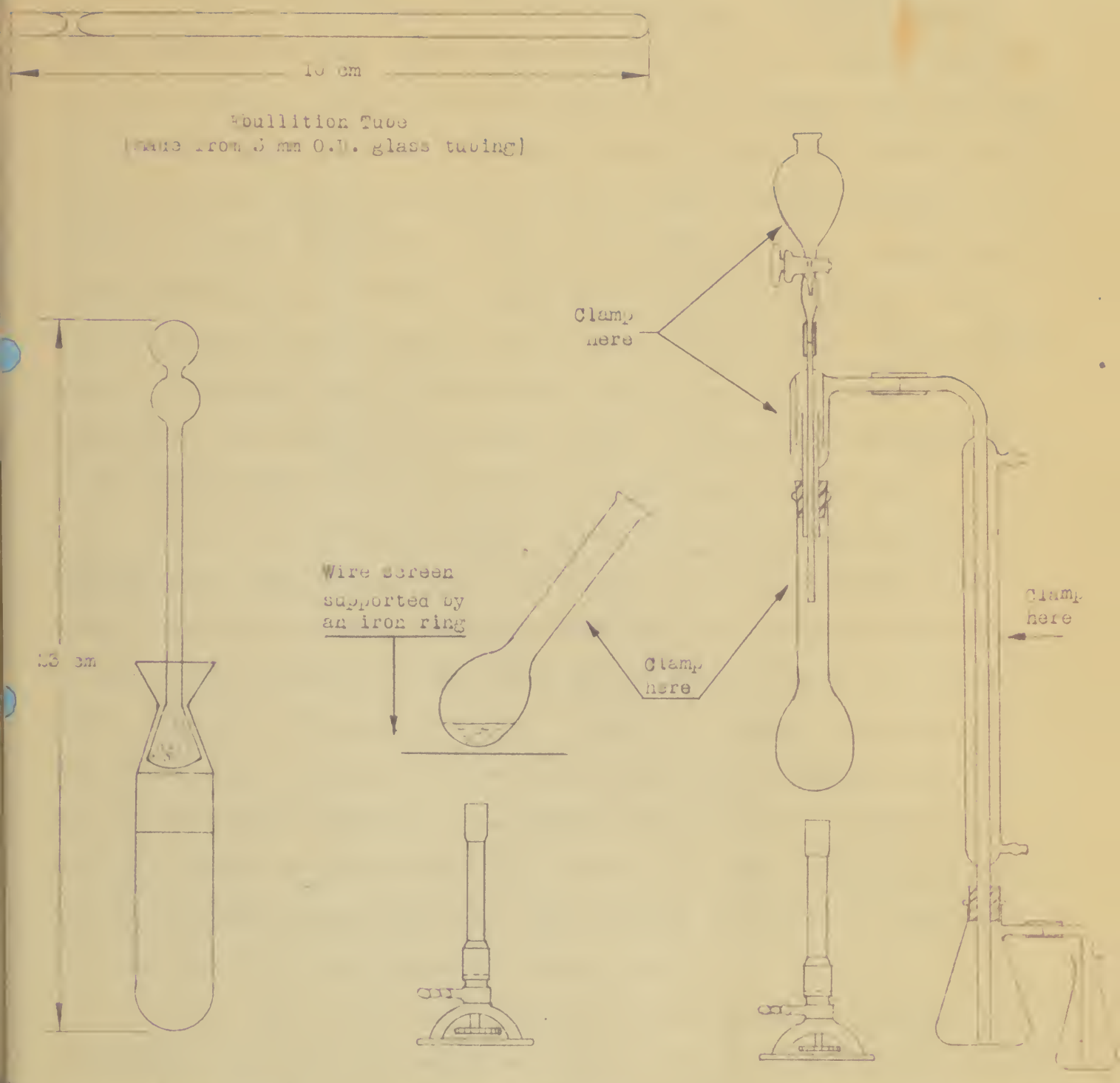


Figure 14. Apparatus for the Determination of Nitrogen

forcing the stopper to the bottom of the Leiboff tube. Immediately withdraw the stopper to the closed position and wash the stopper and the sides of the tube with 1-2 ml of cold HI (Note 4). Allow the closed tube to warm to room temperature and then proceed to the second sentence of the next paragraph.

Add 0.1 ml of 50% H_3PO_2 and 2-3 ml of colorless 7 F HI (Note 2) to the Leiboff tube so as to wash down the sides and stopper (Note 4). Suspend the closed tube by a string in a bath at 120-130° C (Note 5) for 30 minutes; swirl the contents of the tube occasionally during the heating. Remove the tube from the bath, let it stand 2-3 minutes, then cool it under a stream of water. Loosen the stopper, add 8-10 ml of water to the tube and mix the solution (Note 6). Using a dropper with a long capillary tip, transfer the solution to a 100 ml Kjeldahl flask; with the aid of a dropper, wash the tube with three 3 ml portions of water. Use the minimum number of additional 3 ml portions of water (usually about two portions more) necessary to rinse the tube of any solid material. Collect all of the washings in the Kjeldahl flask, and wash the neck of the flask with 1 ml of water.

Add 1 g of $CuSO_4.K_2SO_4$ catalyst (Note 7) to the HI solution in the Kjeldahl flask, then add 4 ml of 18 F H_2SO_4 (Note 8). Swirl the mixture until a uniform solution is obtained. Evaporate the solution over a Bunsen burner (Note 9) with constant swirling until all the iodine is removed, or until the residual volume is 8-10 ml. Then place the flask in position for digestion (see Fig. 14) and heat until the solution has become a clear green color. (Caution: Note 10.) Add 1 ml of 18 F H_2SO_4 dropwise to the Kjeldahl flask and heat the flask so that the H_2SO_4 refluxes in the lower part of the neck of the flask. Continue the digestion for 20 minutes longer (Note 11). Allow the flask to cool for at least 5 minutes, then cool it to room temperature with tap water.

Slowly add 50 ml of water (Caution: Note 12) to the H_2SO_4 solution in the Kjeldahl flask. Place an ebullition tube (see Fig. 14) in the flask and connect the flask to a distilling apparatus (see Fig. 14) which has been recently steamed out (Note 13). Heat the flask until 2-3 ml have distilled and discard the distillate

(Note 14). Adjust the 125 ml receiving flask, which contains the 15 ml of water, so that the tip of the condenser just touches the level of the water. Place the 50 ml bubble trap flask, which contains 5 ml of water, in position. Heat the solution in the flask to boiling and flush the air out of the system (Note 15). While the solution in the flask is kept just boiling, add, from the dropping funnel, 10 ml of 50% NaOH diluted to 20 ml with distilled water (Note 16). Take care to add it slowly enough so that foaming does not occur. When the solution in the flask has become alkaline, as shown by the appearance of a brownish turbidity, increase the heating while the remainder of the NaOH is being added, and collect 15 ml of distillate (Notes 17 and 18). Then remove the bubble trap flask, lower the receiving flask until the tip of the condenser is 2-3 cm above the level of the solution in the receiving flask, and collect about 5 ml more of distillate (Note 19). Finally wash the outside of the condenser tip with 1 ml of water (Note 20).

Add to the solution in the receiving vessel exactly 2 drops of 0.2% methyl red indicator. (Yellow color: presence of nitrogen. Note 21.) Prepare a comparison solution having the proper end-point color by adding to a 125 ml flask 5-7 mg of NH_4Cl, 0.06 ml of 0.2% methyl red indicator, and a volume of distilled water equal to that in the distillate. Boil the comparison solution for 20-30 seconds (Note 22). Titrate the cool distillate solution with standard 0.06 F HCl until the color of the solution matches the color of the hot comparison solution. Then boil the distillate solution for 20-30 seconds (Note 23). Again titrate the hot solution to the end-point color. Prepare a blank of the reagents (Note 24).

From the volume of acid used, calculate the per cent of nitrogen in the sample (Note 25).

Notes.

1. For the methods of handling liquid and solid samples see Note 6, P. I-A. For handling gaseous samples see Informal Report No. 83.

2. If the color of the 7 F HI is deeper than pale yellow, warm the HI and add 50% H_3PO_3 slowly dropwise until the solution is colorless.

3. The ice-hydrochloric acid bath is prepared by adding concentrated technical grade HCl to ice in a beaker.

4. The washing is efficiently performed by adding a portion of the solution to the extended lip of the closed tube and then releasing the stopper slightly to allow the solution to enter the tube.

5. A "bakery pan oil" or glycerine or dibutylphthalate or H_2SO_4 bath may be used if the temperature is carefully controlled by means of a variably controlled hot-plate or Variac type transformer in series with a conventional hot-plate.

A bath which boils at the proper temperature is prepared by adding about 250 g of technical grade $CaCl_2$ to 250 ml of water. If this bath is used, add hot water from time to time to replace the water removed by vaporization.

6. Since highly toxic phosphine may be liberated when the tube is opened, this and the subsequent transfer operation should be carried out under a hood.

If salicylic acid-acetic acid reagent has been added in P. VII-A, salicylic acid may precipitate when the water is added.

7. The catalyst is prepared by thoroughly grinding together in a mortar 10 parts by weight of K_2SO_4 to 1 part of $CuSO_4.5H_2O$.

8. The H_2SO_4 is conveniently added by tilting the Kjeldahl flask and allowing the acid to flow down the neck of the flask.

9. Carry out the evaporation and digestion under a hood since I_2, H_2S, and SO_2 are evolved. A wooden test tube clamp is convenient for handling the hot Kjeldahl flask.

10. Compounds with high carbon content cause the H_2SO_4 solution to foam during the digestion. Therefore, if excessive foaming occurs, the Kjeldahl flask should be swirled to break up the foam, and heated moderately until the tendency to foam is reduced.

Rotate the flask and swirl the solution occasionally during the digestion so that the refluxing solution washes down the sides of the flask.

The green color appears after 15-40 minutes. The time depends upon the type and carbon content of the compound, and upon the rate of heating.

11. Do not heat longer than 40 minutes after refluxing has begun, since otherwise ammonia may be lost.

12. The first portions of water should be added slowly while the solution is kept swirling; otherwise the H_2SO_4 will spatter. The neck of the flask should be pointed away from the analyst.

13. The apparatus must be steamed out from time to time in order to remove alkali from the glass. Steam out the apparatus as follows:

> Fit a 100 ml Kjeldahl flask containing 50 ml of water to the apparatus and drain the cooling water out of the condenser. Boil the water so that steam issues from the condenser for 5 minutes. (The water should drain evenly from the walls of the condenser, leaving no droplets. If this is not the case, detach the condenser, clean it thoroughly, and steam out the apparatus again.) Remove the flask and turn on the condenser water.

14. A grayish solid in the condenser may be iodine or sulfur. These elements, if not removed during the distillation, are steam distilled from the acid solution during this preliminary distillation.

15. Air is known to be out of the apparatus when air bubbles cease appearing in the receiver.

16. The 50% NaOH should not contain much carbonate. It is prepared by dissolving a known weight of reagent NaOH sticks in an equal weight of water. The solution should be allowed to stand for a few days to allow the precipitated Na_2CO_3 to settle, or the Na_2CO_3 may be immediately centrifuged off.

17. The amount of distillate collected can be estimated by comparing the volumes with a known volume of water in a 125 ml flask.

18. If the solution in the bubble trap sucks back into the receiving flask because the boiler solution cools momentarily, increase the flame under the boiler and lower the redeiving flask a few millimeters below the end of the condenser. Then add another portion of water to the bubble trap. If the Bunsen burner is provided with a protecting mantle, more uniform heating can be obtained.

The solution in the receiving flask is rarely drawn back into the boiler if the receiving flask and the condenser are properly arranged, and if the boiler solution is not allowed to cool.

19. The second portion of distillate is collected for the purpose of washing the condenser.

The volume of the solution left in the Kjeldahl flask should be greater than 30 ml after the completion of the distillation, otherwise salts will precipitate and cause troublesome bumping. If, during the distillation, it is thought that the amount of solution left after distillation will be less than 30 ml, add portions of water through the dropping funnel. Add the water slowly enough so that the boiler solution does not cool excessively.

20. There is no necessity to titrate the solution in the bubble trap unless the boiler solution was allowed to foam extensively. The presence of ammonia may be detedted by adding 0.01 ml of methyl red indicator: a yellow color indicates ammonia. If the solution in the bubble trap does contain ammonia, combine it with the solution in the receiving flask before beginning the titration.

21. If no nitrogen or only a small amount was present in the sample, the distillate may be acid due to CO_2 which was originally present in the NaOH as Na_2CO_3. In this case the solution will be red and small amounts of nitrogen will be masked. Therefore, regardless of an orange or red solution, continue with the procedure.

22. The solutions are boiled to remove CO_2.

23. If the distillate solution becomes yellow when heated or while being boiled, immediately titrate with the standard acid to the end-point color. Then continue to boil the solution.

24. Prepare a blank of the reagents as follows:

> To a 100 ml Kjeldahl flask add 2-3 ml of 7 F HI, 0.1 ml of 50% H_3PO_2, and 4 ml of 18 F H_2SO_4. Perform the digestion and distillation as outlined in the procedure.
>
> To the "reagent blank" distillate add 2 drops of 0.2% methyl red indicator and then boil the solution for 20-30 seconds. Titrate the solution to the first pink color with standard 0.06 F HCl. Determine an end-point correction for this titration as follows: boil a volume of water equal to that of the "reagent blank" distillate for 20-30 seconds. Add 2 drops of 0.2% methyl red indicator and titrate the solution with standard 0.06 F HCl to a match of the pink color obtained for the "reagent blank" distillate.

The net correction for the blank on the reagents is equal to the volume of acid used for the "reagent blank" distillate minus the volume of acid used for the end-point correction. This net correction, whether positive or negative, is to be subtracted, with attention to the sign of the correction, from the volume of acid used for the nitrogen sample.

25. One ml of 0.06 F HCl corresponds to 0.84 mg of nitrogen.

P. VII-A Quantitative Determination of Nitrogen in Samples Containing Nitrates

The following procedure is provided for those cases in which the sample to be analyzed may be an organic ester of nitric acid or may be an inorganic nitrate. The sample is first heated with salicylic acid in glacial acetic acid. By this treatment, the salicylic acid is nitrated (by the nitrogen present as nitrate). The solution containing the nitrated salicylic acid is then treated by the modified Kjeldahl procedure (P. VII) by which nitro compounds (and also azo compounds, hydrazones, and others) are first reduced to amines (by the hydriodic acid) and the amino nitrogen then converted to ammonium sulfate by the conventional Kjeldahl digestion.

Weigh 15-30 mg of the sample (see Note 1, P. VII) into a dry 25 ml Leiboff urea tube (see Fig. 14).

If the sample in the Leiboff tube is a high boiling liquid which has been weighed by means of a capillary dropper, or if it is a solid, proceed to the second paragraph below.

If the sample is contained in a glass capsule, add 1 ml of the salicylic acid-acetic acid reagent (see Appendix I) to the tube and cool the tube in an ice-hydrochloric acid bath (see Note 3, P. VII . Crush the glass capsule by carefully forcing the stopper to the bottom of the Leiboff tube. Immediately withdraw the stopper to the closed position and wash the stopper and the sides of the tube with 1-2 ml of cold salicylic acid-acetic acid reagent (Note 4, P. VII). Allow the closed tube to warm to room temperature and then proceed to the second sentence of the paragraph below.

Add 2-3 ml of salicylic acid-acetic acid reagent to the Leiboff tube so as to wash down the sides and stopper (see Note 4, P. VII). Suspend the closed tube by a string in a bath at 120-130° C. (see Note 5, P. VII) for 30 minutes; swirl the contents of the tube occasionally during the heating. Remove the tube from the bath, let it stand 2-3 minutes, then cool under a stream of water. Loosen the stopper, and add 3 ml of 7 F HI (see Note 2, P. VII) so as to wash the sides and stopper of the tube. Treat the mixture in the tube by P. VII, beginning with the second sentence of the third paragraph.

P. VIII

Detection and Estimation of Silicon

This detection and estimation depends upon the formation of a blue color when silicomolybdate is reduced. Arsenomolybdate and phosphomolybdate also produce blue colors when reduced; however, under the conditions of this procedure, the rate of reduction of these compounds is so slow that arsenic and phosphorus do not interfere.

Place a red filter in a colorimeter and adjust the instrument to read zero with a blank of distilled water contained in a 10 ml graduated colorimeter tube (see Operation 7, Appendix V, regarding the use of the colorimeter). Empty the colorimeter tube and pipet into it 1 ml of the Fusion Solution (Note 1). Add

7 drops of 6 F HCl, then add with a pipet 1 ml of 1.0 F NaCl (Note 2). Using 1 F NaOH and 1 F HCl as may be required, carefully adjust the pH of the solution to 3 as indicated by wide range indicator paper (Note 3).

Pipet into the tube 2 ml of monochloracetic acid-sodium monochloracetate buffer solution and 2 ml of 0.6 F ammonium molybdate (Note 4). Mix the solution well. (Yellow color: presence of silicon, arsenic, or phosphorus. Note 5.) Let the solution stand just one minute (Note 6). Pipet 2 ml of 1 F $Na_2S_2O_5$ (Note 4) into the tube, dilute to exactly 10 ml with distilled water, and mix well. (Blue color: presence of silicon. Note 7.)

If silicon is present, place the tube in the colorimeter and read the scale just 60 seconds after the Na_2SO_3 was added (Note 6). From the calibration graph, calculate the amount of silicon in the sample (Notes 8 and 9).

Notes.

1. The Fusion Solution, because it rapidly dissolves silica from ordinary or Pyrex glass, should have been stored in a paraffined bottle (see Note 27, P. I-B).

2. All solutions used in this determination should be stored in Pyrex bottles; further, those bottles containing alkaline solutions should be paraffined.

3. The success of this procedure is dependent upon the proper adjustment of the pH of the solution. Care should be taken to rinse the sides of the tube free of any added acid or base with the solution in the tube (see Operation 5, Appendix V). If the pH is less than 2.4 before reduction with Na_2SO_3, phosphate and arsenate will interfere by causing finally a blue color similar to that caused by silicate. If the pH is greater than 3.0, the color from silicate will develop slowly.

4. This operation can be carried out more rapidly (see Note 6) if the solution is blown out of the pipet, rather than allowed to drain out. The resulting error in the volume of the solution added is negligible.

5. In case arsenic and phosphorus are absent, the yellow color arising from 10 gamma or less of silicon can be seen. In case either arsenic or phosphorus (or both) is present, any yellow color developed here must not be interpreted as indicating the presence of silicon.

6. The time allowed is critical. It should be not less than 60 seconds and not more than 70 seconds. If a large quantity of phosphorus is present, and the solution is allowed to stand too long before addition of Na_2SO_3 a yellow precipitate of ammonium molybdophosphate may separate. If this happens, the Na_2SO_3 should be added at once, and the solution quickly centrifuged. If the resulting centrifugate is clear, a colorimetric reading can be made with little error, providing that it is made 1 minute after the addition of the Na_2SO_3.

The molybdenum blue color, formed after the addition of Na_2SO_3, is usually stable for at least two minutes, but it will sometimes darken appreciably during the second minute, especially in the presence of phosphate, arsenate, or other ions, and in all solutions which do not have the optimum pH (2.4-2.7) before the addition of Na_2SO_3.

7. Under the conditions of this estimation, the color from 5 gamma of silicon can be seen when compared with a similar tube containing water. As much as 2 mg each of arsenic and phosphorus and 0.5 mg of fluorine do not interfere.

8. Use the following procedure for constructing the graph:

To a 15 ml graduated centrifuge tube add 0.35 ml of 6 F HCl and 1.0 ml of 1 F NaCl. Pipet into the colorimeter tube used to set the colorimeter to zero (see Operation 7, Appendix V), the desired quantity of Na_2SiO_3 test solution. Add by means of a pipet 0.35 ml of 6 F NaOH (from a paraffined bottle). Pour the contents of the centrifuge tube into the colorimeter tube, and mix well. Proceed as directed in the fourth sentence of this procedure beginning with "adjust the pH of the solution to 7".

It is suggested that the following amounts of silicon be used in the construction of the graph: 200, 150, 100, 75, 50, 25, and 10 gamma. Plot the colorimeter readings as ordinates against silicon content (as gamma of silicon) as abscissae.

9. If the analysis of a 1 ml portion of the Fusion Solution results in a colorimeter reading of more than 500, and if the amount of silicon must be known accurately, a second 1 ml portion of the Fusion Solution should be diluted to 10 ml in a volumetric flask with freshly prepared 2 F NaOH, and a suitable aliquot portion taken for analysis by this procedure.

The error in the amount of silicon found by this procedure should be not greater than 5-10 per cent of the amount present.

P. IX The Quantitative Determination of Carbon and Hydrogen

In order to obtain greater clarity of presentation this procedure has been divided into sections as indicated below:

P. IX-A Assembly of Apparatus
P. IX-B Performing Blank Analysis
P. IX-C Equilibration of Combustion Tube Filling
P. IX-D The Analysis of Solid and Liquid Compounds

See Appendix VI for a list of the apparatus and reagents required to perform these procedures.

Preliminary Statement: A weighed sample is combusted in a stream of oxygen; by this means the carbon in the sample is converted to carbon dioxide and the hydrogen to water. By successive passage of the effluent gases through two absorption tubes containing suitable solid absorbents for water and carbon dioxide, these compounds are quantitatively absorbed and determined by the increase in weight of their respective absorption tubes. Complete oxidation of the sample is ensured by passing the gases over platinum and copper oxide at an elevated temperature. Volatile combustion products of elements other than carbon and hydrogen which might increase the weight of the absorption tubes are removed by suitable solid absorbents placed in the combustion tube. Thus, halogen is removed by silver, sulfur trioxide by silver and lead dioxide (hereafter designated by the commercial name, "lead peroxide"), and oxides of nitrogen by "lead peroxide".

P. IX-A Assembly of Apparatus

Secure the oxygen cylinder to the table top in order to eliminate the possibility of its being knocked over and attach the needle valve to the cylinder. Assemble the pressure regulator (A)[1], fill the outer cylinder about half full with distilled water (Note 1) and with glass and rubber tubing (a) connect the outlet of the needle valve with the inlet tube of the pressure regulator (Note 2).

1 Letters placed after the names of pieces of equipment refer to the photographs appended to this procedure.

Place a plug of glass wool in each compartment of the Kraissl drying tube (B) and with a glass rod push the plugs to the far end of the tube (Note 3). With the plugs in position invert the tube and fill each compartment with anhydrous granular magnesium perchlorate until the level of the end of the dividing wall is reached. Place a third plug of glass wool in the remaining space in order to hold the absorbent in position when the tube is inverted. Warm the stopper, apply a thin film of Krönig's cement to the warm ground surface of the stopper and quickly insert it in position with a twisting motion to form a firm transparent seal (Note 4). Connect the outlet tube of the pressure regulator to the inlet tube of the drying tube with a short length of black gum rubber tubing (b) (Note 5).

Place a plug of glass wool in each compartment of the Kraissl tube equipped with the bubble counter (C) and with a glass rod push the plugs to the far end of the tube (Note 3). Invert the tube and fill the compartment adjacent to the bubble counter with ASCARITE until the level of the dividing wall is reached. Fill the other compartment with anhydrous granular magnesium perchlorate; place a third plug of glass wool in the undivided space of the tube, coat the warm surface of the stopper with Krönig's cement and immediately insert the stopper in position with a twisting motion to form a firm transparent seal (Note 4). Introduce concentrated sulfuric acid into the bubbler, with the aid of a capillary pipette, until the level of the liquid is approximately 1 - 2 mm above the tip of the inlet tube (Note 6). Connect the inlet tube of the bubble counter with the outlet tube of the drying tube previously prepared with a short length of black gum rubber tubing (c) (Note 5) and clamp the tube in position.

Straighten the side arm of the combustion tube (D) with the aid of an oxygen-gas flame and place the combustion furnace (E) in position in front of the gas train previously assembled. Place the combustion tube (D) in the furnace in such a manner that the distance from the beginning of the constricted portion of the combustion tube to the nearest end surface of the combustion furnace is 7.5 cm.

Move the furnace and tube on a line parallel to the assembled gas train until the side arm of the combustion tube and the exit tube of the gas train are near each other. Procure a piece of 4 mm O.D. glass tubing (d), make a right angle bend at one end, cut the arms to the proper length and fire polish the ends (Note 7). Remove the combustion tube from the furnace, place the heating mortar (F) in position adjacent to the end face of the combustion furnace, previously nearest to the constricted end of the combustion tube, and align the orifice of the mortar with the opening in the combustion furnace (Note 8).

Form a plug of tangled silver wire approximately 2 cm in length and place it in the combustion tube in such a manner that a few strands of wire extend into the capillary portion of the combustion tube (Note 9). Compress the plug with the aid of a footed glass rod, until the length of the plug is 1.5 cm. Place ignited asbestos fiber in the combustion tube and gently tamp it with the footed glass rod until the length of the plug is 0.5 cm (Note 10). Place the combustion tube in position in the furnace and mortar, and connect the side arm of the combustion tube with the gas purifying train using the piece of glass tubing previously prepared for that purpose (d). Connections can be made with black gum rubber tubing provided that a minimum amount of rubber surface is exposed to the gas (Note 5).

Turn on the furnace (E) and mortar (F), allow the mortar to attain its apparent equilibrium temperature (Note 11) and adjust the variable transformer of the combustion furnace to bring the temperature of the combustion furnace to 700°C (Note 12). Mount the Mariotte bottle assembly (G) on a stand (Note 13) at a height sufficient to allow the graduated cylinder (H) to be placed under the delivery tube, and place 900 ml of distilled water in the bottle (Note 14). Charge the remaining drying tube (J), known as the terminal drying tube, with separate portions of anhydrous granular magnesium perchlorate and ASCARITE using plugs of glass wool to hold the absorbents in position. Bend a short length of 4 mm O.D. glass tubing (i) to form a right angle bend and fire polish the ends. Insert one arm of the

bent tube in a one hole black rubber stopper and insert the assembly in the wide opening of the terminal drying tube. Connect the other end of the terminal drying tube to the inlet of the siphon tube of the Mariotte bottle assembly with a length of black gum rubber tubing (f) (Note 15).

Insert a red gum rubber stopper (g) in the open end of the combustion tube and connect the capillary tip of the combustion tube to the inlet of the terminal drying tube with a length of black gum rubber tubing. With the stopcock of the siphon tube (K) closed, cautiously open (Note 16) the needle valve of the oxygen cylinder until the gas is escaping from the pressure regulator (A) at a slow but steady rate. Now lower the delivery tube of the Mariotte bottle (L) until a horizontal position is reached and place the graduated cylinder (H) under the outlet (Note 17). Cautiously open the stopcock of the siphon tube (K) and allow the water to flow from the bottle into the cylinder until the effluent stream reaches a constant rate (Note 18). Then with the aid of a graduated 15 ml centrifuge tube and a watch determine the rate of flow using a time interval of one minute. If the rate is found to be 10 - 15 ml/minute the density of the asbestos plug in the combustion tube is satisfactory. If the rate is either greater or less than this value it is necessary to remove the combustion tube from the assembly and to rectify the situation either by compressing or by loosening the plug until the desired rate is attained (Note 19).

If the rate is found to be satisfactory, remove the combustion tube from the furnace, allow the tube to cool, and place a 3 cm zone of granular "lead peroxide" in the tube (Note 20). The "lead peroxide" is held in place by next introducing a 0.5 cm zone of ignited asbestos fiber taking care not to compress the filling in place. Now place the tube in the furnace, allow it to come to thermal equilibrium, connect it to the remainder of the system as described in the paragraph above and determine the rate of flow of gas again. If the rate is found to be 7 - 10 ml/minute, withdraw the tube from the furnace and allow it to attain room temperature

(Note 21). Now introduce a 2 cm zone of silver wire (Note 22) and then a 2.5 cm zone of platinum gauze (Note 23). With the platinum gauze in position, incline the tube at an angle of 45° and carefully introduce an 11.5 cm zone of wire-form copper oxide by allowing the wire to slide down the walls of the tube. Rotate the tube while bringing it to a vertical position to consolidate the copper oxide zone and place a final 2.5 cm zone of platinum gauze in position adjacent to the copper oxide zone. Place the combustion tube in the furnace and mortar, connect it with the rest of the system, allow it to attain thermal equilibrium (Note 24), and determine the rate of flow of gas through the system.

If the directions given above have been carefully followed, the rate will be found to be 5-7 ml/minute. If the rate is less than or exceeds this value, change the hydrostatic head in the pressure regulator (A) (Note 25) to bring the observed rate within the recommended limits. Disconnect the Mariotte flask assembly (G) from the system and allow oxygen to pass through the combustion tube for 12-24 hours with the mortar at approximately 180°, and the combustion furnace at 700° C in order to condition the combustion tube filling (Note 26).

The absorption tubes (M and N) are procured and thoroughly cleaned and dried (Note 27). Place a plug of glass wool (Note 28) in the far end of each absorption tube taking care not to compress the plug to such an extent that the ball valves cannot function properly. Fill the water absorption tube (M) with anhydrous magnesium perchlorate; leave sufficient space at the open end of the tube for a second glass wool plug. Carefully swab the inner ground surface with a piece of cotton, carefully warm the ground surface of the stopper in a gas flame, apply a thin film of Krönig's cement to the warm surface and insert the stopper in position with a twisting motion to form a firm transparent seal. During this final operation, take care that the ball valves are aligned so that both are either open or closed at the same time. Fill the carbon dioxide-absorption tube (N) in the same way using ASCARITE as the absorbent (Note 29); take care to keep the weight of the carbon dioxide-absorption tube to within

25 mg of the weight of the water-absorption tube in order that one tare may be used for both tubes. Finally, prepare three pieces of special impregnated micro rubber tubing (P), 2.5 cm in length, for connecting the absorption tubes to the rest of the system and make suitable supports (Q) from No. 24 Nichrome wire for the absorption tubes (Note 30).

Notes.

1. Pregl recommends 5 percent sodium hydroxide instead of water; however, this is not necessary. In order to lessen the amount of water vapor in the effluent oxygen stream, sulfuric acid of specific gravity, 1.14, may be used. In assembling the pressure regulator, the inner cylinder should be placed in such a position that two thirds of the length is within the outer cylinder and the distance from the bottom of the inner cylinder to the surface of the liquid is approximately 5-6 cm. It is recommended that the pressure regulator be clamped to a stand in order to minimize breakage.

2. Care should be taken to make all connections so as to minimize the rubber surface in contact with the gas. This is essential because rubber tubing may give off organic vapors which will contaminate the oxygen. Artificial aging of the rubber tubing, by heating in vacuo with vaseline, has been recommended but is not essential if connections are essentially glass to glass or glass to metal.

3. The plugs are introduced in order to prevent the absorbent from getting into the inlet and outlet tubes. The size of the plugs should not be excessive nor should they be packed too solidly.

4. The stopper may be removed by first warming the joint with a gas flame to soften the cement.

5. A glass to glass contact should be made in order to minimize the amount of rubber surface exposed to the gas. The drying tube is held in position with an extension clamp and stand.

6. As sulfuric acid will attack rubber connections, care should be taken to avoid contamination of either the inner or outer surface of the inlet tube for a distance of approximately 1 cm from the open end.

7. It will be found desirable to constrict the end abutting the side arm of the combustion tube to the diameter of the side arm in order to facilitate connection.

8. It is imperative that the mortar and furnace be properly aligned in order that undue strain will not be placed on the combustion tube.

9. In view of the difficulty of introducing the plug in such a manner that a few strands of wire extend into the capillary portion, a recommended alternative procedure is to procure a piece of silver wire approximately three quarters the length of the constricted portion of the tube and introduce it into the constricted end of the tube until the far end of the wire is in contact with the compressed plug of silver wire.

10. This plug should not be tamped in position too vigorously. It is easy to compress it if it is found to be too porous, but it is time consuming to loosen it if it is too dense.

11. The thermometer can be held in position in the thermometer well of the heating mortar with a few pieces of asbestos fiber. The temperature of the mortar should be approximately 180°C; however, the actual temperature is not very critical provided that it is constant.

12. It is suggested that the maximum voltage be passed through the furnace until the temperature, as indicated by the meter, is 800°C. The voltage is then reduced to approximately 80 volts. It should not take longer than 15 - 20 minutes to attain the desired temperature.

13. The bottle may be mounted on a stand with the aid of a ring and a clamp or may be supported on a tripod. Sufficient space along the axis of the combustion tube should be allowed in order to accommodate the absorption tubes.

14. Before introducing the water, the delivery tube is placed in a nearly vertical position. A small amount of copper sulfate may be added to the water to prevent the growth of algae.

15. Sufficient tubing should be provided to permit connection of the terminal drying tube with the capillary tip of the combustion tube during the preliminary testing operations described in the next paragraph of the procedure.

16. It is advisable to break the connection between the needle valve and the pressure regulator when first opening the needle valve.

17. During the preliminary testing operations the graduated cylinder may be replaced by a flask or bottle of comparable capacity.

18. This may be determined by collecting the effluent stream of water in a 15 ml centrifuge tube and noting the time required to collect 10 - 15 ml of water. To test the system for leaks temporarily remove the connection between the pressure regulator and the inlet of the Kraissl tube and seal the latter with a piece of rubber tubing closed at one end with a piece of glass rod. If the system if free from leaks, the flow of water from the delivery tube of the Mariotte bottle will stop after a few seconds. To prevent loss of water from the Mariotte bottle when the system is disconnected, close the stopcock on the siphon tube.

19. If the plug is either compressed or loosened, care should be taken to keep the length of the plug at the recommended 0.5 cm length, by adding or removing asbestos as required.

20. In introducing the "lead peroxide" the granular, dust free particles are allowed to slide down the walls of the combustion tube inclined at an angle of 45°. The material is then consolidated by rotating the tube while bringing it to a vertical position. The lead peroxide sticking to the walls of the combustion tube above the lead peroxide zone is removed by swabbing the tube with a wad of cotton attached to a piece of nichrome wire.

21. If the rate is less than the recommended value loosen the asbestos plug holding the "lead peroxide" filling in place and again determine the rate of flow.

22. This filling is prepared in the same manner as the previous silver zone by forming a plug of tangled wire.

23. This zone is prepared by rolling a 1" x 6" strip of platinum gauze into a compact cylinder whose O.D. is equal to the I.D. of the combustion tube. On placing this and the previous zone in position care should be taken not to compress the zone previously introduced.

24. A steady state is usually reached within 15 minutes.

25. It will be found more convenient to add or withdraw the liquid with a pipette after raising the cover of the regulator than to change the position of the wire cylinder.

26. This conditioning is necessary in order to remove volatile impurities present in the various zones but is necessary only when first setting up the apparatus or when a new combustion tube filling is placed in the tube.

27. Distilled water and acetone are suitable for this operation.

28. Pyrex glass wool should be used and care should be taken to leave no strands of glass in such a position that they might interfere with the operation of the ball valve. Alternatively, one can interpose a disk of coarse filter paper between the glass wool and the end of the ball valve assembly.

29. Some authors recommend that a desiccant be placed in this tube but this has been found not to be necessary for centigram operations.

30. It is recommended that thin strips of gummed paper 2-3 mm wide be placed on the cylindrical surfaces adjacent to the end faces of each piece of rubber tubing to provide a surface for marking the tubing.

P. IX-B

Performing a Blank Analysis

Clean the capillary side arms of the absorption tubes (H and N) with a small wad of cotton (Note 31) in order to remove traces of lubricant, dust and rubber that may be present on both the inside and outside surfaces (Note 32). Grasp one end of the water-absorption tube with a moist chamois skin (Note 33) and systematically wipe the other half of the tube with a second chamois skin (Note 34). When this operation is completed grasp the wiped end of the tube with the chamois and repeat the process. Do not touch the tubes with the bare fingers from the time the wiping is begun until the tubes are weighed. After the water-absorption tube is wiped, place it on a support, made from a piece of nichrome wire (Note 35), and located near the balance, and proceed to wipe the tare and the carbon dioxide-absorption tube in exactly the same way. Allow the wiped tubes to remain on the stand for ten min-

utes and then weigh the water-absorption and the carbon dioxide-absorption tube in the order named, using the wiped tare (Note 36). Weigh the tubes to the nearest ± 0.05 mg (Note 37). It is recommended that the analyst repeat the above operations until successive weighings after wiping agree to within ± 0.10 mg (Note 37).

Lubricate three 2.5 cm lengths of impregnated rubber tubing (P) by passing a wire dipped in glycerine (Note 38) through the bores, followed by a wad of dry cotton held on the end of a piece of wire (Note 31). Attach a length of the rubber tubing so prepared to each of the capillary side arms of the water-absorption tube; push the side arms into the tubing for a distance of 1.25 cm (Note 39). Place the third length of rubber tubing on one of the side arms of the carbon dioxide-absorption tube and connect the two absorption tubes; take care to place the ends of the capillary side arms in an abutting position and to align the ball valves so that all of them are in the same position (Note 40). Now interrupt the flow of oxygen through the apparatus by turning off the needle valve on the oxygen cylinder and connect the free side arm of the water-absorption tube to the capillary tip of the combustion tube; take care to place the ends of the capillary tubes in an abutting position and to place the ball valves in an open position (Note 41). Finally connect the free capillary side arm of the carbon dioxide-absorption tube to the terminal drying tube.

Carefully open the needle valve of the oxygen cylinder (Note 16); then open the stopcock of the siphon tube on the Mariotte bottle, and allow 250 ml of oxygen to pass through the system at the rate of 5-7 ml/minute (Note 42). Close the stopcock of the siphon tube, break the connection between the end of the terminal drying tube and the siphon tube, disengage the absorption tubes from the combustion tube, - keep the length of rubber tubing on the side arm of the water-absorbing tube, - and insert a piece of glass rod (Note 43) in the position previously occupied by the capillary tip of the combustion tube.

Allow the absorption tube-terminal drying tube assembly to stand for 10-15 minutes to attain room temperature, disengage the absorption tubes, clean the

capillary side arms, wipe the tubes, and weigh them as described above. The weights of the absorption tubes should not differ from the previously determined weights by more than 0.10 mg (Note 37). If this agreement is obtained, the apparatus and technique may be considered to be satisfactory for use. If not, the operations should be repeated until the operator attains the requisite technique (Note 44).

Notes.

31. The cotton is held on a piece of nichrome wire whose end has been knurled or bent to form a very small hook.

32. The capillary side arms should be carefully examined, preferably with a lens, to be sure that they are clean and free from cotton lint.

33. The chamois skin should be moist and not wet. The strip of skin is placed on the thumb and index finger and the tube then grasped.

34. The wiping should be systematic and gentle. Vigorous wiping is to be avoided as this may lead to the formation of an electric charge on the surface of the glass.

35. It is suggested that the support be made to hold three absorption tubes.

36. An attempt should be made to develop a routine in weighing the absorption tubes so that a definite schedule is maintained.

37. This value is based upon the assumed use of a macro analytical balance.

38. In spite of its hydroscopicity, glycerine is the most satisfactory lubricant.

39. In order to facilitate entry, it may be necessary first to insert a piece of fire polished glass tubing of the same size as the side arms of the absorption tubes into the glycerined piece of tubing and to heat the tubing so prepared in an oven at 160° for 10-20 minutes. After cooling and removing the glass tubing, the bore will be of the right size to fit the side arms of the absorption tubes with proper snugness.

40. It is imperative that the absorption tubes be connected in exactly the same way each time the operation is performed. As an aid to remembering, a notation may be written on the paper slips placed on the ends of the rubber tubing (see Note 30 above). In addition, an arrow should be placed on the paper indicating the direction of the gas stream.

41. The other end of the combustion tube should be firmly held during this operation.

42. Minor adjustments in the rate of flow can be made by altering the hydrostatic head in the pressure regulator or by lowering the delivery tube of the Mariotte bottle. Once changes are made they should not be further altered during

the course of an analysis.

43. A piece of glass tubing sealed at both ends is equally satisfactory.

44. Failure to attain the recommended agreement may be due to improper cleaning of the side arms of the absorption tubes, improperly lubricated rubber tubing in the sense that too much lubricant has been allowed to remain in the tubing, failure to make glass to glass connections, insufficient conditioning of the combustion tube filling, failure of the gas purifying train, and improper technique in handling and weighing the absorption tubes.

P. IX-C Equilibration of Combustion Tube Filling

If the apparatus has been allowed to stand unused for more than 2-3 days (Note 45) or if the combustion tube filling has not previously been used in an actual combustion, it is advisable to combust a 10-15 mg sample of sucrose in order to equilibrate the combustion tube filling. It is not necessary to collect the products of the combustion.

Turn on the furnaces and allow the combustion furnace to reach a steady temperature of 700°C (Note 46). Procure and clean a platinum boat (Note 47) and place approximately 10-15 mg of sucrose in the boat; store the charged boat on a Corwin block. Open the needle valve on the oxygen cylinder (Note 16) and connect the capillary tip of the combustion tube directly to the inlet of the siphon tube of the Mariotte bottle. Open the stopcock on the siphon tube, lower the delivery tube to a horizontal postition, place a cylinder under the outlet and adjust the flow of gas through the apparatus until the rate is 5-7 ml/minute. Then remove the stopper from the end of the combustion tube and with a forceps, place the charged platinum boat in the tube. With a piece of nichrome wire advance the boat into the tube until it is approximately 5 cm from the combustion furnace (Note 48). Form a 1" x 6" strip of platinum gauze into a roll (Note 49) and by grasping it with a forceps heat the roll to redness in an oxidizing gas flame. When it has cooled to room temperature, place it in the combustion tube and advance it towards the boat until the near end is 1-2 cm from the boat (Note 50). Stopper the combustion tube, place the cylinder of nichrome gauze over the roll of platinum gauze, close the stopcock on the siphon tube return the water in the cylinder to the Mariotte bottle, and then open the stopcock

on the siphon tube with the cylinder in position.

With a Bunsen burner begin to heat the zone covered by the nichrome gauze cylinder, carefully observing the bubble counter. At first, the rate of gas flow will diminish; it will then return to normal as a steady state is reëstablished. If the flow of gas through the bubble counter ceases, temporarily discontinue heating the combustion tube. When the normal rate is regained, advance the flame and nichrome gauze towards the sample with the aid of a piece of nichrome wire. This operation is to be governed by constant observation of the bubble counter; when the rate of flow diminishes, thus indicating an increase of pressure in the combustion tube, the forward progress of the burner and gauze should be stopped and, if necessary, the burner removed (Note 51). In the course of 10-15 minutes advance the nichrome gauze and burner to the point of maximum travel; then remove the burner, withdraw the nichrome gauze to a position back of the platinum gauze (Note 52), replace the burner and repeat the operation.

Remove the burner and allow oxygen to sweep through the system until approximately 250 ml of water have been collected in the graduated cylinder (Note 53). Close the stopcock on the siphon tube, remove the rubber connection from the end of the combustion tube, and turn off the oxygen (Note 45).

Notes.

45. When the apparatus is not in use, the system should be sealed by placing a piece of rubber tubing closed with a glass rod on the capillary tip of the combustion tube.

46. Before turning on the furnaces be certain that the cylinder of nichrome gauze has been slipped on the combustion tube and placed adjacent to the side arm.

47. The boat should be cleaned by immersing it in boiling 6 F nitric acid, and then by heating to redness in an oxidizing flame.

48. Care should be taken to keep the boat upright during this operation.

49. This roll is prepared in the same manner as were the platinum plugs placed in the combustion tube filling.

50. This plug functions as a baffle which prevents or limits the backward distillation of the sample during its ignition. The platinum gauze baffle is much more satisfactory than the glass baffles previously recommended.

51. This operation is p critical of all the operations encountered in this procedure. The sample and bubble counter should be closely observed and every attempt should be made to keep the ignition as smooth as possible without wasting time.

52. Care should be taken not to place the nichrome gauze cylinder in a position that would lead to heating of the rubber stopper.

53. The amount herein specified (250 ml) is sufficient for 10-15 mg samples; for larger samples the amount of water collected should be increased proportionately.

P. IX-D The Analysis of Solid and Liquid Compounds

Turn on the furnaces (Note 54) and assemble the complete combustion train including the absorption tubes (Note 55). Open the needle valve on the oxygen cylinder (Note 16) and after the operating temperatureof the furnaces has been attained, determine the rate at which oxygen is flowing through the apparatus. If the rate is found to be 5-7 ml/minute, proceed as directed in the next paragraph. If the rate is not satisfactory, adjust either the pressure regulator or the delivery tube of the Mariotte bottle until the specified rate is observed (Note 56).

Close the stopcock on the siphon tube of the Mariotte bottle and disengage the absorption train by first breaking the connection with the capillary tip of the combustion tube; leave the rubber connection on the side arm of the water-absorption tube. Insert a piece of glass rod in the space previously occupied by the capillary tip of the combustion tube and then break the connection between the terminal drying tube and the siphon tube of the Mariotte bottle. Set the absorption train aside for 10-15 minutes and prepare the sample for analysis.

Clean a platinum boat and ignite it (Note 47); place the boat in a weighing piggie whose external surface has been wiped with a moist chamois. Place the piggie on the balance pan (Note 57) and allow it to remain there for 5 minutes before it is weighed. Remove the weighed piggie containing the empty boat from the balance pan, place it on the floor of the balance case (Note 58) and remove the stopper with the aid of moist chamois skins. Withdraw the boat by grasping the handle with a forceps and place it on a clean, dust free surface (Note 59). With the aid of a micro spatula, transfer the sample to the boat until the requisite quantity has been added

(Note 60). Return the charged boat to the piggie, replace the stopper, place the assembly on the balance pan and weigh after five minutes. Then set the sample to one side on the floor of the balance case.

Disconnect the absorption tubes, carefully clean the side arms, wipe the exterior surfaces and weigh them. Lubricate the impregnated rubber connections with glycerine, and again assemble the absorption train; leave the connection between the water-absorption tube and the combustion tube until last. If the system is gas tight, oxygen will not pass through the bubble counter. Place the piggie containing the sample on a Corwin block, and place the block near the fore end of the combustion tube. Remove both the rubber stopper sealing the end of the combustion tube and the platinum baffle (Note 61), open the piggie, withdraw the charged boat and immediately place it in the combustion tube with the aid of a forceps. Using a nichrome wire advance the boat to a position approximately 5 cm from the end of the combustion furnace. Ignite the platinum baffle and place it in position; stopper the combustion tube.

Return any water in the graduated cylinder to the Mariotte bottle, lay the copper heating wire of the mortar (R) on the inlet to the water-absorption tube, and open the stopcock of the siphon tube of the Mariotte bottle. Place the nichrome wire cylinder over the platinum baffle and heat the former with a hissing Bunsen flame extending about 2 cm above the gauze. The sample now characteristically melts, sublimes, or decomposes. The behavior of the sample and of the bubble counter serve as a guide to the rate at which the flame may be advanced. If the bubbles stop, or even slow down appreciably, the flame must be moved back until they resume their normal flow speed. Advance the wire gauze, followed by the flame, only a few mm at a time; often a ring of distillate or sublimate forms and advances down the tube as the flame is moved forward. Excercise special care in moving the flame and gauze up to large drops of liquid which may suddenly vaporize, and also in bringing the burner near the hot mouth of the furnace. Advance the gauze and flame to the mouth of the furnace during the course of 15 minutes. Then remove the burner, return the gauze to a posi-

tion 1 cm behind the platinum baffle and repeat the operation a second time but at a greater speed. Usually, five minutes will be found to be satisfactory.

Sometimes stubborn carbonaceous residues are formed which may require the use of the hottest flame on the naked tube (Note 62). If such residues are allowed to cool momentarily and then strongly heated, they will often ignite with a shower of sparks. Towards the end of the combustion the capillary inlet of the water-absorption tube should be examined to make certain that no water condenses at this point (Note 63). If water does condense in the capillary inlet, thus indicating improper functioning of the extension heater, the water may be driven into the tube by the careful application of a hot file or wire to the surface of the inlet near the condensed droplets (Note 64). When the ignition has been completed, allow an additional 100 ml of oxygen to sweep through the combustion tube; during this time the analyst may weigh out a second sample (Note 65). Under normal circumstances not more than 200 ml of oxygen will pass through the system during the course of an analysis (Note 66). When the sweeping-out process is completed close the stopcock on the siphon tube of the Mariotte bottle and disconnect the absorption train (Note 67). Remove the rubber stopper sealing the combustion tube, withdraw the boat, and examine it for the presence of ash with the aid of a lens. If ash is absent ignite the boat and return it to a weighing piggie for subsequent use. If ash is present, weigh the boat and record the amount of ash. Replace the rubber stopper and disconnect the absorption tubes. Clean, wipe, and weigh the tubes (Note 68). From the increase in weight of the tubes calculate the percent of carbon and hydrogen in the sample (Note 69).

Notes.

54. The combustion furnace should be maintained at a temperature of 700°C.

55. The absorption tubes are placed in the train in order that they may be filled with dry oxygen. This operation is necessary only if the absorption tubes have not been used within the preceding hour.

56. Once the pressure regulator and the delivery tube have been adjusted they should not be touched during a series of analyses. It is recommended that the major adjustment be made by changing the hydrostatic head in the pressure regulator as it is not advisable to have more than a very slight vacuum at the terminal end of the train.

57. Moist chamois skins may be used for transfering the piggie to the balance pan provided that only the tail is grasped.

58. It is assumed that the floor of the balance case is kept scrupulously clean.

59. A piece of glazed tile or a piece of glazed paper (note book) may be used.

60. The procedure described for the analysis of solids can be applied to the analysis of liquids if weighing pipets are used.

This technique is described in P. I and is also considered in detail in the text Organic Quantitative Microanalysis by Niederl and Niederl.

The amount of sample will be dependent to some extent upon the anticipated percentage of carbon. However, as a general practice it is suggested that the sample weight be kept within the limits of 15-25 mg in order that the sample may be weighed with sufficient accuracy on a macro balance.

61. When the stopper is removed, gas will pass through the bubble counter rather rapidly due to the decrease in resistance.

62. Excessive use of a hot flame on the bare combustion tube may cause the tube to crack long before the end of the useful life of the combustion tube filling.

63. Condensation of water droplets in the side arm will also cause an increased resistance to the flow of oxygen; their presence may therefore be suspected if the rate of gas flow diminishes for no other immediately apparent reason.

64. Merely touching the hot file or wire to the surface is sufficient. Care should be taken not to heat the ground surfaces unnecessarily as this will cause the cement to soften.

65. It is suggested that a second piggie be used so as to retain the use of the first piggie for the boat in the combustion tube.

66. Every effort should be made to use no more than the recommended volume because the use of larger amounts may cause error due to impurities in the oxygen. It cannot be emphasized too often that successful results are obtained only when the same routine is used for blank determinations (no sample) and for determinations on known and unknown compounds.

67. The procedure used here is identical with the one described previously in connection with the blank determination.

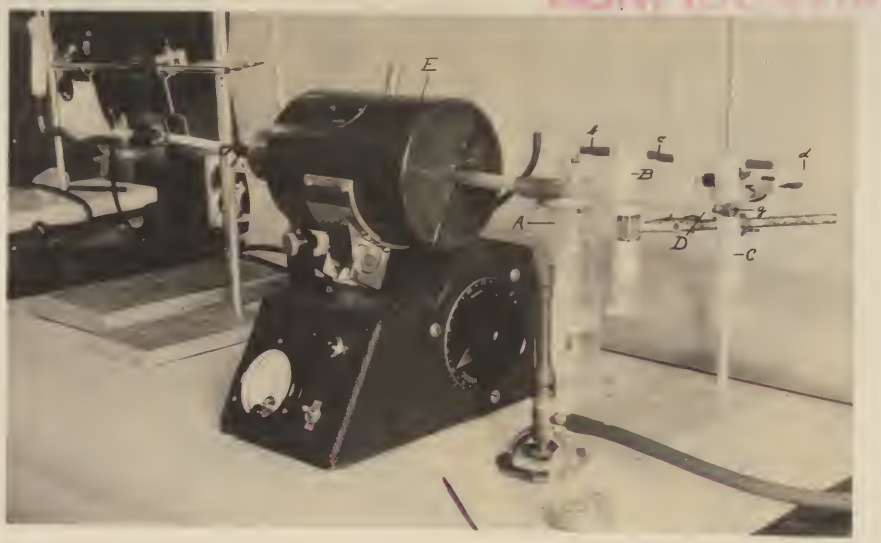
68. Each analysis in a series requires about 80 minutes from one weighing of the absorption tubes to the next.

89. For calculating the percentage of carbon and hydrogen, logarithms and factors may be conveniently used as indicated below:

Percentage of Hydrogen	Percentage of Carbon
Log weight H_2O	Log weight CO_2
Plus log factor (2.04375)	Plus log factor (2.43573)
Minus log weight sample	Minus log weight sample
Equals log % H	Equals log % C

If ash is found, a slide rule is sufficiently accurate for the computation:

$$\% \text{ Ash} = \frac{100 \text{ (weight of residue)}}{\text{(weight of sample)}}$$



P. X The Estimation of Carbon (Wet Combustion Method)

A weighed sample is heated with an anhydrous sulfuric, phosphoric, chromic, and iodic acid mixture in a stream of CO_2-free air, and the carbon dioxide evolved is absorbed in sodium hydroxide. The carbonate thus formed is precipitated as barium carbonate and determined acidimetrically. The method is accurate to within ± 0.04 mg of carbon.

This procedure is designed primarily for the analysis of solid compounds, especially derivatives of CW agents. The apparatus is less complicated, can be assembled much more rapidly, and single analyses can be made much more quickly than with the combustion train used in P. IX. However, this method has not been tested on the wide variety of compounds which the dry combustion method is known to handle; therefore, difficulty may be encountered with some compounds. For example, some compounds containing a CN group have given off HCN when treated with the combustion mixture; hence, quantitative carbon values for such compounds could not be expected if this method is used.

H has been satisfactorily analyzed by this procedure, by weighing the liquid from a pycnometer into the combustion tube. Although it seems reasonable that other liquids of similar or lower volatilities can be satisfactorily analyzed by this method, time has not been available in which to collect experimental data regarding the maximum volatility of substances which can be adequately handled by this procedure. Compounds more volatile than H can probably be analyzed by cooling the combustion tube and sample during the flushing operation.

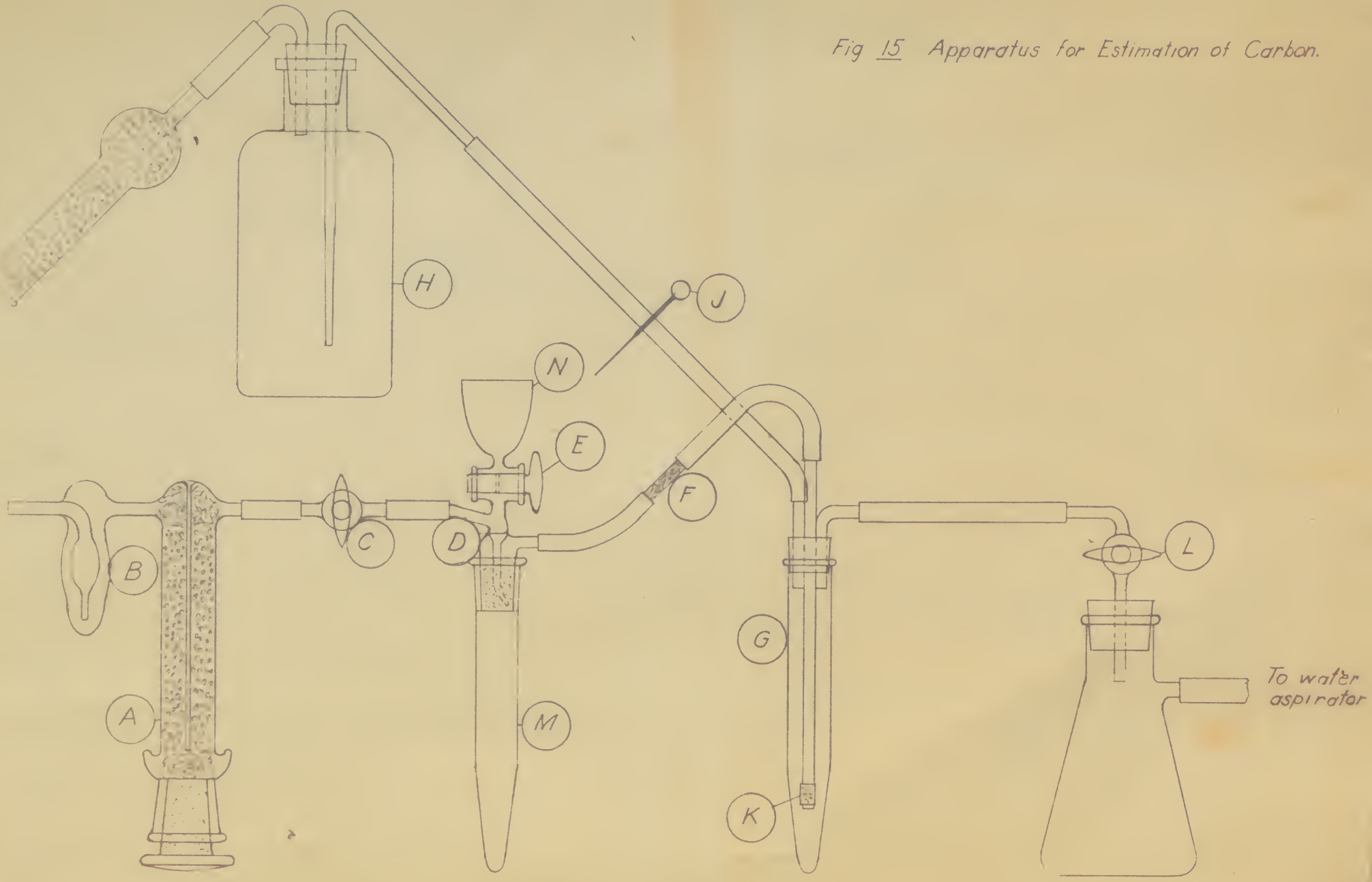
Assembly of the Apparatus:

Assemble the apparatus as shown in Fig. 15. Clean, dry, and reserve a glass stoppered 15 ml centrifuge tube (Tube M) (Note 1). Pack the Kraissl absorbtion tube A on both sides with 20-30 mesh Ascarite or soda lime (Note 2). Add sufficient concentrated H_2SO_4 to the bubble counter B to immerse the inlet tube about 2 mm.

Connect micro stopcock C (Note 3) to tube A and head D, lengths of clean, dry rubber tubing; leave stopcock C in the open position. Lubricate stopcock E with concentrated H_3PO_4 and leave it in the closed position (Note 4). Connect tube F to the outlet of head D with a 2-3 inch length of rubber tubing. Fill tube F with glass wool moistened with 3-4 drops of distilled water (Note 5).

Bore three holes in a No. 1 rubber stopper. Through one hole, pass a

Fig 15 Apparatus for Estimation of Carbon.



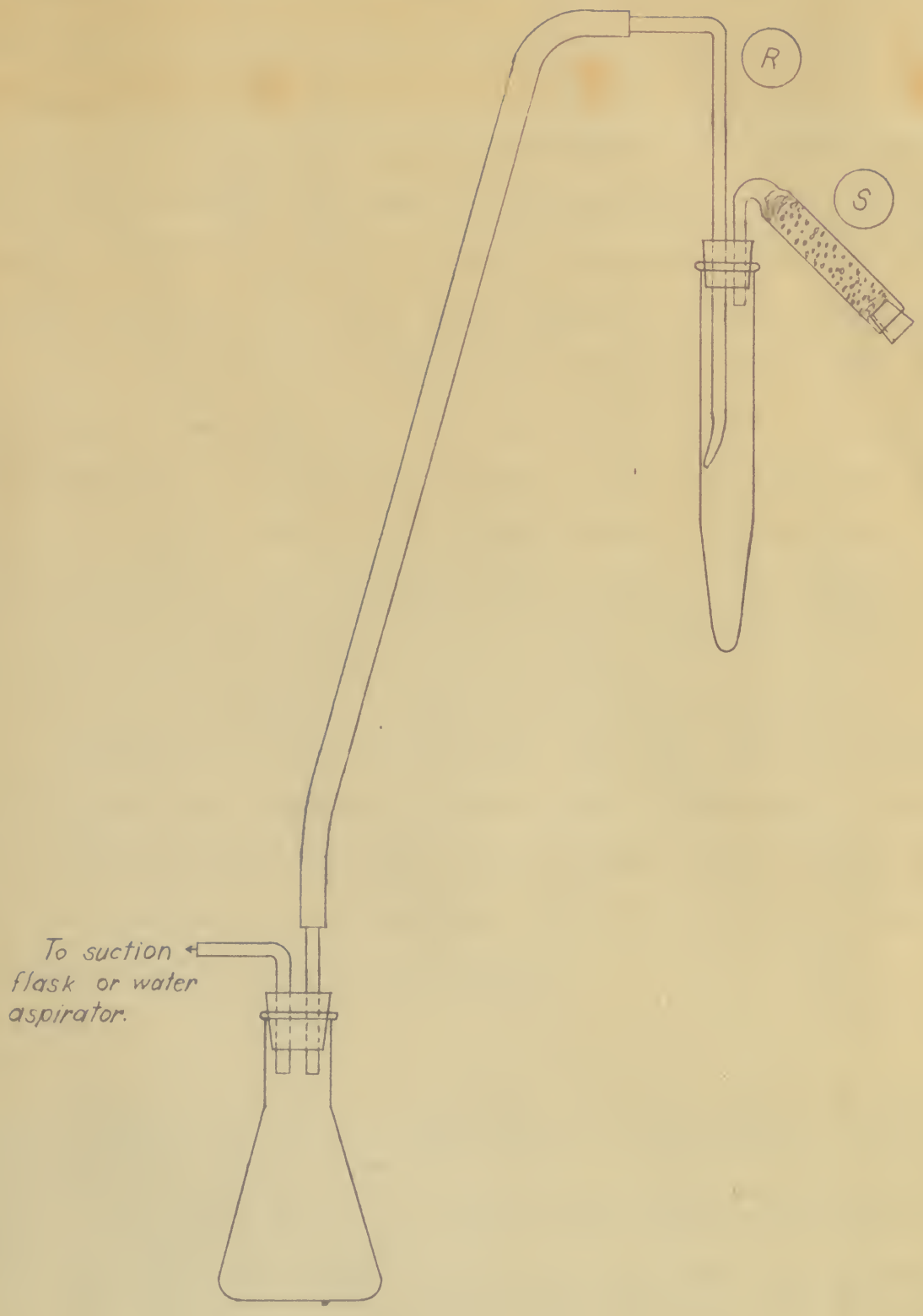


Fig 16 Vacuum Siphon

short length of 4 mm glass tubing which has a 1 mm tip. Connect this tube to the delivery tube of the storage bottle H (which contains sodium hydroxide-barium chloride reagent, 0.5 F in NaOH and 0.004 F in $BaCl_2$), and attach pinch clamp J to the connecting tube. By applying a slight pressure through the soda lime tube of bottle H, force solution from H until it fills the delivery tube, then close clamp J. Moisten the glass tubing which carries the disperser K (Note 29, p. 108) with a drop of glycerine and insert the tubing in the rubber stopper (Note 6); connect the disperser inlet tube to tube F with a 4-5 inch length of rubber tubing. Insert in the third hole of the stopper a 4 mm glass outlet tube and connect it to micro stopcock L (Note 3). Pass the other arm of the stopcock (L) through a No. 3 rubber stopper, then fit the stopper into a 125 ml suction flask. Connect the side arm of the suction flask to a water aspirator with clean, dry rubber tubing (Note 7). Just before attaching the 15 ml centrifuge tube (G) to the 3 hole stopper assemble, open clamp J and allow 2-3 ml of the NaOH-$BaCl_2$ reagent to flush out the connecting tube.

Finally, assembly the vacuum siphon (Fig. 16). Place tube R (Note 8) and special soda lime tube S (Note 9) in a two hole No. 1 rubber stopper. Connect tube R to the 50 ml flask with about 2 feet of rubber tubing. When the vacuum siphon is used, disconnect the rubber tubing from the outlet of tube G and connect that tubing to the outlet of the 50 ml flask.

Notes.

1. The tube, which receives the sample, should be cleaned with hot CrO_3-H_2SO_4 solution, rinsed, dried, and protected from dust by inverting in a clean beaker or by stoppering with a glass stopper.

2. Place a plug of glass wool in each compartment of the Kraissl tube to protect the inlet and outlet tubes. Another plug of glass wool should be placed between the filling and the stopper.

3. Stopcocks C and L should be lubricated with a thin film of grease.

4. The stopcock should turn easily. Do not force the stopper as it may lock.

5. If it is known that the apparatus does not contain fluorine, tube F may be omitted from the apparatus. This tube is inserted to remove HF which would attack the inside of the disperser and so clog the pores that the disperser could not be flushed out.

A clean tube and filling should be used for each run because the acid produced by the absorption of SO_3 lowers the efficiency of HF absorption.

6. Since the disperser is moved in the stopper during each run, the inlet tube should be kept moveable in the stopper. The disperser should be rinsed out with dilute HCl and water and should be dried before being used.

7. Solid or liquid which may have been deposited in the connecting tube by spray from previous runs should be washed out and the tube should be dried.

8. Tube L is made from 4 mm tubing drawn to a 1 mm tip at one end. Allow a 15 cm length from the tip, then make a right angle bend which will aid in moving the tube in the stopper.

9. Special soda lime tube S consists of a 3 inch length of 10 mm tubing attached to 2 inches of 4 mm tubing bent as shown in Fig. 16. The 4 mm tubing can be sealed to 10 mm tubing or a section of the 10 mm tubing can be collapsed and drawn to 4 mm diameter.

Place a plug of glass wool at the narrowed end of the 10 mm section and fill the tube with Ascarite or soda lime. Cap the tube with a plug of glass wool and a cork which has been grooved on the side with a file.

Procedure for the Analysis of Solid Substances

Weighing the Sample

Carefully weigh (Note 10) a 10-12 mg sample of the substance for analysis into a clean, dry 15 ml glass stoppered centrifuge tube (M).

Moisten the ground surface on head D with concentrated H_3PO_4; then attach tube M, turning the tube until a firm seal is obtained.

Flushing and Filling the Apparatus

Turn on the water aspirator and slowly open stopcock L until the rate of air flow through bubble counter B is 3-4 bubbles per second. After 4-5 minutes, carefully open clamp J and admit NaOH to tube G to within 3-4 cm of the top of the tube. Do not admit the NaOH so rapidly as to cause liquid to back up into the disperser tube. Pour 5-6 ml of combustion solution (see Appendix I) into cup N, and adjust the rate of air flow to 1-2 bubbles per second. Close stopcock C (Note 11) and immediately open stopcock E. When most of the liquid has entered tube M close stopcock E (Note 12), and immediately open stopcock C.

Combustion of the Sample and Absorption of Carbon Dioxide

By means of stopcock L adjust the rate of air flow through counter B (Note 13) to 3-4 bubbles per second. Watch the action of bubble counter B (Note 14) and first warm the upper portion of the combustion mixture with a micro burner, then the lower part. When gas is evolved, control the heating so that bubble counter B indicates positive flow or is at equilibrium (Note 15). If liquid starts to back

up in B (Note 16), quickly close stopcock C and cease heating for a few seconds until the evolution subsides. Open stopcock C and continue to boil the combustion mixture. Heat the mixture so as to obtain vigorous gas evolution (Note 17).

After 5-6 minutes of heating (Note 18), remove the flame and fill cup N with concentrated H_2SO_4. Close stopcock C and open stopcock E. When the liquid level in tube M is 2-3 cm below the inlet tube of head D, close stopcock E (Note 12) and open stopcock C. Ascertain that the rate of air flow through B is still about 3 bubbles per second.

Removal of the Absorbing Tube

When 3-4 minutes has elapsed since filling tube M with acid, slide the disperser inlet tube up through the stopper until the disperser is a cm or more above the solution. Close stopcock L, then disconnect the rubber tubing from the disperser inlet tube. By means of a long capillary dropper fill the disperser inlet tube with CO_2-free distilled water (Note 19). Carefully open stopcock L and draw the water through the disperser. (Do not draw air through the disperser.) Close L and remove the stopper from the centrifuge tube (Note 20). Rinse off the bottom of the stopper and the disperser with a few drops of CO_2-free water, then rinse down the walls of tube G with a few drops of the water.

Precipitation of the Carbonate

With a dropper or pipet add 1-1.5 ml of barium chloride reagent (1 F in $BaCl_2$, and 0.001 F in HCl) (Note 21) to tube B and immediately stopper the tube with a No. 1, one hole rubber stopper which is fitted with a short piece of 0.5 mm capillary tubing (Note 22). Place the centrifuge tube in a bath of boiling water for 2-3 minutes. Replace the rubber stopper with a rubber centrifuge tube cap, then centrifuge until the solution is clear.

Washing the Precipitate

Mount the centrifuge tube (G) firmly in a buret clamp. Moisten tube R in the vacuum siphon apparatus so that it moves freely through the rubber stopper.

Adjust tube R so that the tip projects only 3-4 cm below the rubber stopper. Remove the cap from the centrifuge tube and immediately insert the rubber stopper. Carefully open stopcock L until solution is drawn slowly out through R. With a twisting motion push R down as the solution level recedes until the tip of R is just above the precipitate (Note 23); no precipitate should pass into R. Remove the stopper from the centrifuge tube and rinse down the walls of the tube with 1-2 ml of CO_2-free water.

Add 1 drop of 0.2% phenolphthalein to the mixture and stir up the precipitate. By means of a dropper, add 0.05 F HCl, stirring the mixture intermittently to break up the precipitate (Note 24), until the phenolphthalein color becomes light pink; then add 8-10 drops of 1 F $BaCl_2$ (Note 25) and 1 drop of 1% Aerosol OT solution. While stirring, add 0.05 F HCl dropwise until the mixture is white, then add just 1 drop of the acid in excess. Rinse any precipitate from the stirring rod into the centrifuge tube. Centrifuge until the solution is clear, and remove and discard the solution with a dropper.

Titration of the Carbonate

Rinse down the walls of the tube with 1-2 ml of boiled water. Add 1 drop of 0.2% phenolphthalein and 3-4 drops of 1 F $BaCl_2$ and then stir up the precipitate (Note 26). If necessary add 0.05 F HCl dropwise with stirring, until the mixture is white, then add 1 drop of 0.1% methyl orange. From a microburet, add standard 0.2 F HCl and stir intermittently until the solution is pink. Place the tube in a bath of boiling water for about 1 minute, stirring to aid evolution of CO_2. If necessary add more standard acid until the pink color remains, then add about 0.1 ml (0.1-0.2 scale divisions) of the standard acid in excess (Note 27). Transfer the solution to a 50 ml conical flask and rinse the centrifuge tube with 2-3 ml of CO_2-free water. While swirling the flask continuously, boil the solution gently for about 1 minute. Cool the solution to room temperature and titrate with standard 0.05 F NaOH. After the methyl orange becomes yellow, continue the titration (2-3 drops) until the pink of the phenolphthalein produces a light orange color; this

last color is the end-point of the titration. From the amounts of acid and base used, calculate the percent of carbon in the compound (Note 28).

Notes.

10. Solids should be handled in weighing tubes (see Note 6 and Fig. 5 in P. I). Hold the combustion tube A in a horizontal position and insert the weighing tube inside it so that the sample is delivered into the tip of the combustion tube. Do not scatter particles of the sample along the combustion tube as the weighing tube is withdrawn. Since the combustion fluid occupies only a third of tube A, particles of sample in the upper part of the tube may not be decomposed.

By removing the damper and carefully recording the swings, the weighings can be estimated to 0.02 mg. In order to obtain this accuracy, the sensitivity of the balance should be 8-10 divisions per milligram.

Although this procedure has been designed primarily for solids, H has been satisfactorily analyzed. L. Liquids of similar or lower volatility may be analyzed by this procedure, using a pycnometer as directed in Note 6, P. I for weighing out the sample. In order to decrease the possibility of loss by evaporation, the sample should be delivered into the very tip of the combustion tube.

11. Stopcock C must be closed during the admission of liquid into tube M; otherwise bubbles of the viscous combustion mixture will be formed in the head (D) and combustion fluid will be blown up into the outlet tube.

12. Cut off the flow of liquids before the last few drops reach the stopcock; no air should be admitted to the apparatus.

13. The rate of gas flow through disperser K should be watched in making the rate adjustment as the main object of the flow regulation is to keep the bubbles from K relatively small. It may be necessary to adjust the rate of flow occasionally if the flow through K is seen to vary appreciable.

14. When liquid backs up in bubble counter B, gas is passing from tube M to tube A. This should be prevented since any CO_2 which reaches tube A will be absorbed and cause error; for this reason it is necessary to observe counter B at all times.

15. Tube M should not be heated in one spot as the oxidation reaction may proceed suddenly and force CO_2 back into tube A. Although it is satisfactory to operate the system so that there is no actual positive flow through B, there must be no reverse flow through B.

16. When the temperature of the combustion mixture is well over 150°, the chromic acid decomposes to give off oxygen. The oxygen evolution is not smooth or easily controlled; therefore, the heat should be applied carefully.

17. The boiling action is needed to completely sweep out the CO_2. Occasional heating at the tip of tube M is desirable because the bubbles formed there will sweep through the entire solution.

18. If the solution in tube M has not turned green by this time because of the decomposition of chromic acid to chromic ion, the mixture has not been heated sufficiently.

19. All distilled water used for rinsing or washing in this determination should be boiled before using in order to eliminate the error due to dissolved CO_2. Boil the water for several minutes and store it in a glass stoppered Pyrex bottle from which portions may be removed to dropping bottles.

20. To prevent absorption of CO_2, do not breathe into the open centrifuge tube.

21. Since diffusion in the solution may be slow, the $BaCl_2$ reagent should be squirted in instead of being added dropwise. Stirring is not necessary if the reagent is injected forcefully.

22. If a metal ring is available (see Fig. 2 B and Note 2, P. XIII), a rubber centrifuge tube cap secured by the metal ring may be used to cap the tube during the digestion.

23. Avoid jarring the apparatus during the removal of solution; otherwise

particles of precipitate may be freed and drawn out.

24. Especially in the case of large amounts of precipitate, as much as 3-4 ml of the 0.05F HCl may be required. Therefore, do not start by adding the acid dropwise but deliver it in squirts through the surface of the solution by means of a fine tipped dropper. Use a dropwise addition when the base is nearly neutralized. It is necessary to keep the time of washing down to 3-4 minutes to avoid absorbing an appreciable amount of CO_2. On the other hand, large local excesses of acid must be avoided, especially on the surface of the solution.

25. Because of the acid in the $BaCl_2$ reagent, the mixture may turn white after adding the $BaCl_2$. In this case do not add any more 0.05 F HCl but proceed directly to the centrifugation.

26. All precipitate adhering to the walls must be scraped off and thoroughly stirred up.

27. For convenience in calculation, it is recommended that the acid titration be stopped exactly on a tenth of a scale division.

28. Percent of carbon = $\frac{\text{ml of acid x formal concentration} - \text{ml of base x formal concentration}}{\text{mg of sample}} \times 600$

29. If the disperser is not available, it can be made by closing, with a piece of glass, one end of a short length of Zircofrax tubing, 12-7P-89, $\frac{1}{4} \times 1/8$, and joining the other end to a length of standard wall Pyrex tubing. The joints are glass.